A STUDY OF THE SYSTEM: ETHYLENE, IODINE AND ETHYLENE DI-IODIDE IN THE ABSENCE OF LIGHT.

By

Ronald B. Mooney, M.A., B.Sc.

Thesis for the Degree of Ph.D.

1929

I Introduction.

Faraday observed that ethylene and iodine combined in sunlight to give ethylene diiodide (Gmelin's Handbook 1853 VIII 363). Regnault found that the combination also took place in diffuse light, and was more rapid if the reacting substances were heated to 50° or 60°C (Liebig's Annalen 15 67).

Slator (J.C.S. 85 1697) studied the decomposition of ethylene di-iodide in aqueous alcohol. He found the velocity of decomposition was increased by bright sunlight and also by the presence of iodide ions.

Villard (Chem.News (1898) 297) carried out some experiments on the effect of ethylene at high pressures on the vapour pressure of iodine, and observed a slow combination to form ethylene di-iodide.

None of these authors mentions experiments on the formation or decomposition of ethylene di-iodide in which care was taken to exclude diffuse light. It therefore remained doubtful whether there was an appreciable dark reaction.

To test this, some crystals of iodine were placed in a glass bulb filled with ethylene at atmospheric/

atmospheric pressure, and the bulb was left in complete darkness for three days. At the end of that time about one half of the iodine had disappeared, and white, needle-shaped crystals of ethylene di-iodide were visible. This was accompanied by a decrease in the pressure of ethylene.

It was thought desirable to carry out quantitative experiments on the dark reaction

$$C_2H_4 + I_2 \rightleftharpoons C_2H_4I_2$$

in which the velocity of the two opposite reactions and also the final position of equilibrium should be studied.

In the course of this work the velocities of formation and decomposition of ethylene di-iodide have been studied both in the gaseous state and in solution in carbon tetrachloride. Values of the equilibrium constant of the gas reaction have been obtained for several temperatures between 10° and 65°C. The vapour pressure of ethylene di-iodide has been measured over the same temperature range.

II Preparation and properties of ethylene di-iodide.

It was thought best to start with the reacting substances in the form of pure solid ethylene di-iodide whenever possible, because ethylene di-iodide is a comparatively inert crystalline substance/

substance, which is much more easily purified and handled than a system consisting of iodine and ethylene gas. The preparation and purification of the di-iodide were therefore conducted with considerable care.

Faraday and other early experimenters prepared $C_2H_4I_2$ direct from C_2H_4 and I_2. This method is too slow in the absence of sunlight.

Semenow (J. 1864 483) described a method in which C_2H_4 is bubbled into a layer of I_2 crystals covered with absolute alcohol.

Spindler (Liebig's Annalen 231 265) described a method in which liquid $C_2H_4Cl_2$ is heated for 120 hours at 75°- 80°C with the calculated amount of crystallised CaI_2.

Semenow's method of preparation promised to be more convenient than Spindler's, so it was always used. The experimental arrangements were as follows:-

Ethylene gas was prepared in the early part of the research by the action of glacial phosphoric acid on ethyl alcohol at 200°C. (Cohen's Theor.Org.Chem. p.249). Later, a cylinder of compressed ethylene was obtained, and proved a much more convenient and easily regulated source of the gas.

The ethylene was dried with $CaCl_2$ but not otherwise/

otherwise purified. It was passed through two gas wash-bottles connected in series. The first wash-bottle contained a layer of 50 - 100 gms. I_2 covered with absolute alcohol, and the second wash-bottle contained about 5 gms. I_2 in alcohol to unite with most of the ethylene which passed through the first wash-bottle uncombined. Ethylene was passed into the first wash-bottle at such a rate that one bubble every three or four seconds passed into the second bottle. Under these conditions, in diffuse light, most of the iodine was converted into ethylene di-iodide in 7 or 8 hours.

The resulting crystals of $C_2H_4I_2$ were filtered, washed with alcohol to remove iodine, and pressed on porous tile to dry.

At this stage, when the crystals contain alcohol as impurity, they decompose readily. After recrystallisation from cold ether they still tend to become discoloured with iodine, but $C_2H_4I_2$ which has been recrystallised from hot carbon tetrachloride keeps very white for days. If these pure crystals are sealed up in a glass tube in an atmosphere of ethylene they show no iodine coloration after seven or eight months.

It was found convenient to seal up the ethylene di-iodide in small tubes, each containing about/

about 5 gms. and to break open one tube at a time, as required.

The melting point of pure ethylene di-iodide was found to be 81° C, which agrees with Aronstein and Kramp's value of 81° - 82°C (Berichte 13 489).

III The decomposition of $C_2H_4I_2$ in presence of mercury.

The decomposition of ethylene di-iodide in presence of mercury is irreversible, because the iodine which is formed is held by the mercury in the form of HgI_2.

Assuming that the decomposition takes place in the gaseous state, the rate of increase of the pressure of ethylene above ethylene di-iodide and mercury should be given as by

$$\frac{d\,P_{C_2H_4}}{dt} = k.\ P_{C_2H_4I_2}$$

So long as any solid $C_2H_4I_2$ remains, $P_{C_2H_4I_2}$ should be constant and equal to the vapour pressure of $C_2H_4I_2$. The graph of pressure against time should be of the form shown in Fig.(1), the discontinuity in the curve corresponding to the total decomposition of $C_2H_4I_2$.

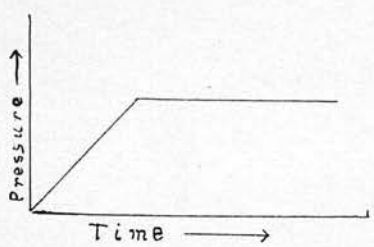


Fig (1)

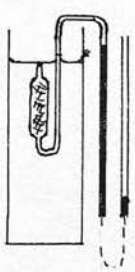


Fig. (2)

Some/

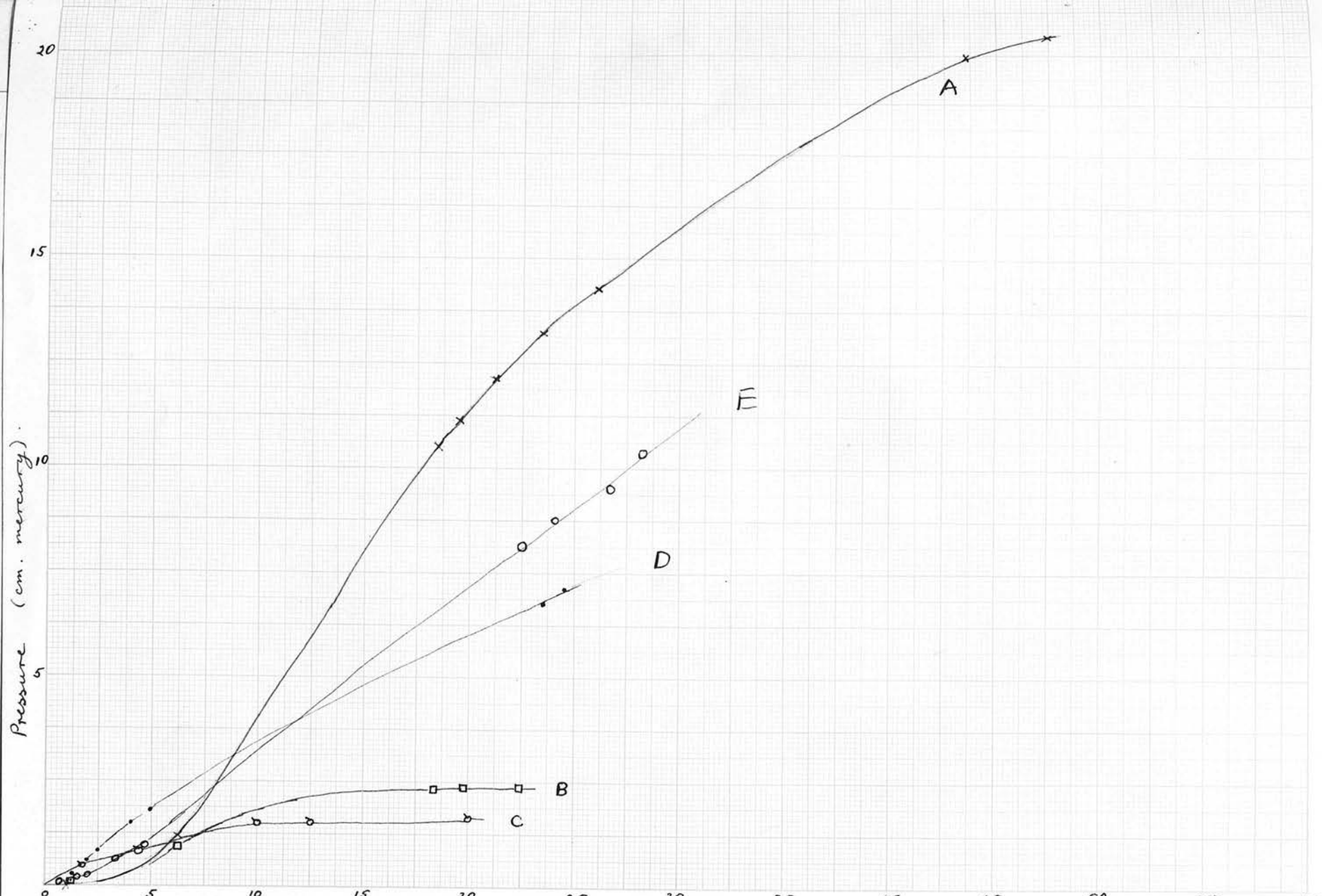

Pressure (cm. mercury).
Time (hours.)
A
B
C
D
E
0
5
10
15
20
25
30
35
40
45
50
55
60

Fig. 3.

Some rough experiments were carried out to test this.

Small quantities (.01 to .2 gm) of $C_2H_4I_2$ were placed in a glass bulb containing a large surface of amalgamated copper gauze and a few drops of mercury (Fig.2.). A mercury manometer was attached to the bulb. The bulb was evacuated with an oil pump, sealed off, and immersed in a 25° thermostat in the dark.

Readings of pressure and time were taken over a period of several days. The results obtained are plotted in Fig (3). The curves show considerable deviations from the expected form.

In most of the curves $\frac{dP}{dt}$ is small at first, then greater, and decreases again towards the end of the curve.

The slow initial rise of pressure is attributed to adsorption of ethylene by the large surface present in the bulb. After the surface is saturated with ethylene the curve becomes approximately a straight line, as seen in the middle part of the curves. The slowing down towards the end may be partly due to the fact that the experiment was not conducted under strictly constant volume conditions, the volume increasing slightly as the mercury was forced down. More important reasons may be 1) that the pressure of $C_2H_4I_2$ was not maintained at the full vapour pressure/

pressure throughout the space, owing to the difficulty of diffusing through the increased pressure of ethylene; or 2) that the reaction is not really a homogeneous gas reaction under the conditions described.

The experiments do not furnish sufficient data to indicate which is the correct explanation of the anomalies. Not much stress is laid on the value of the experiments, because the $C_2H_4I_2$ which was used had only been recrystallised from ether and certainly contained impurities.

Values of $\underline{k}$ obtained from the central (straight line) part of the curves are given in Table I. The vapour pressure of $C_2H_4I_2$ was taken as 0.19 mm. from the results of section VII

The disagreement of the values of $\underline{k}$ are explained 1) if the reaction is homogeneous, by the catalytic influence of impurities; 2) if the reaction is a surface reaction, by the different surfaces present in the different experiments.

Table I.

Curve	$\frac{dP}{dt}$ $\frac{mm.}{min.}$	$Pc_2H_4I_2$ mm.	$k = \frac{1}{Pc_2H_4I_2} \cdot \frac{dP}{dt}$
A	0.12	0.19	0.6
B	0.03	"	0.15
C	?	"	?
D	0.07	"	0.4
E	0.06	"	0.3

IV. The decomposition of ethylene di-iodide in solution.

Lueck (J.Amer.chem.Soc.,47 1240) found that the rate of decomposition of N_2O_5 in CCl_4 and $CHCl_3$ was practically the same as in the gaseous state. It was therefore thought that CCl_4 might be a suitable solvent for the study of the decomposition of $C_2H_4I_2$.

The $C_2H_4I_2$ was purified in the manner described in section II. Commercial CCl_4 was purified by shaking with NaOH, washing with water, drying with $CaCl_2$ and distilling through an 8-bulb still-head.

Preliminary observations showed that the decomposition was very slow at ordinary temperatures, so it was decided to study the reaction at a temperature of 100° C. Even then the decomposition was slow. The solutions of $C_2H_4I_2$ in CCl_4 were sealed up in glass tubes to prevent volatilization.

At intervals of several hours or days a tube was broken open and 10 c.c. of the contents were titrated with sodium thio-sulphate. Preliminary experiments were made which proved that I_2 in CCl_4 can be titrated in presence of $C_2H_4I_2$ provided the titration does not last for more than a few minutes. There is a reaction between $C_2H_4I_2$ and thiosulphate (Slator J.C.S.,85 1298) but it is too slow to affect the titration.

It/

A :- Decomposition in solution containing 2·12 gm. $C_2H_4I_2$ per 100 c.c.
B :- " " " " 1·30 " " " "

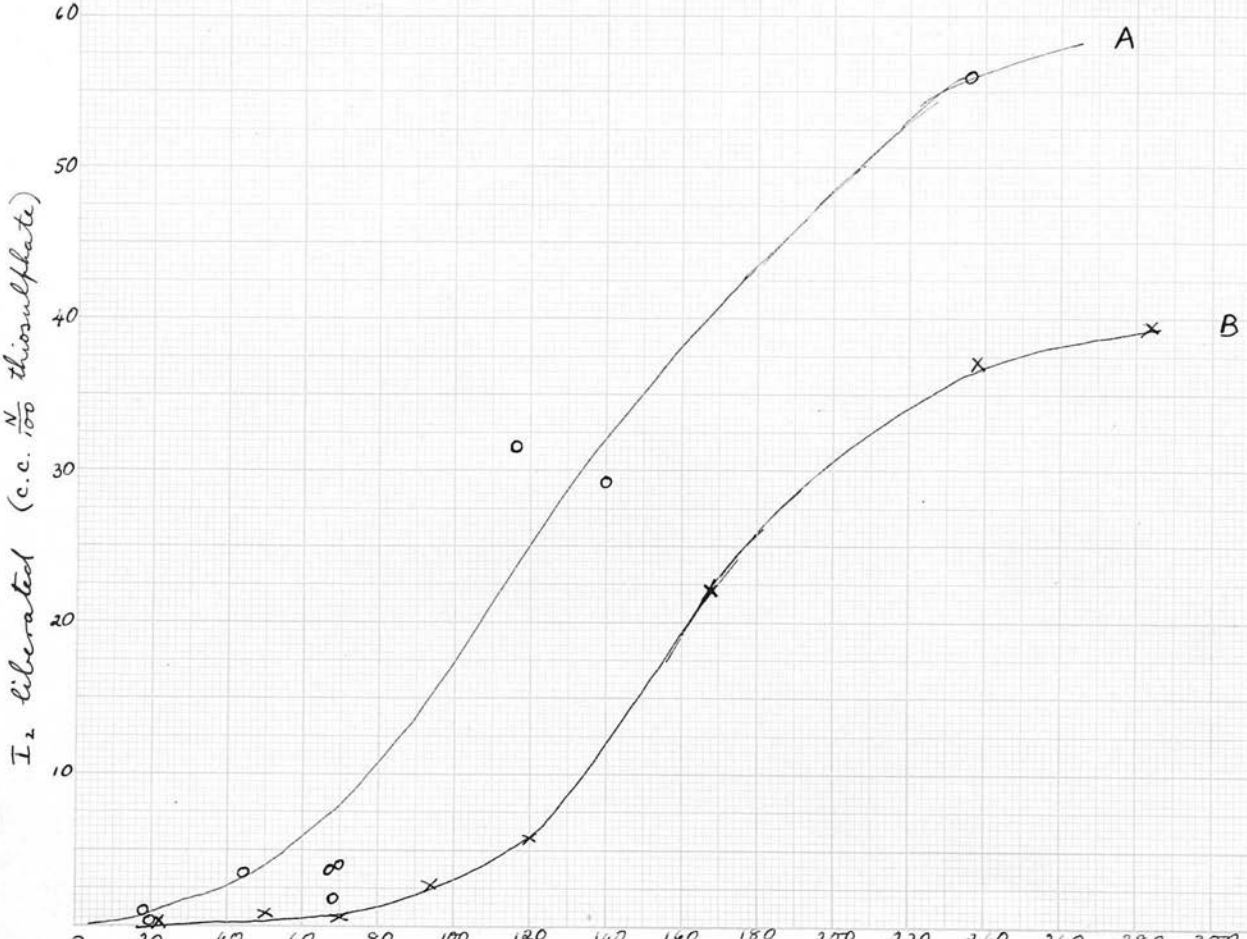


Fig. (4)

It was found convenient to add 25 c.c. absolute alcohol to the CCl_4 solution before titrating, as this facilitates mixing the thiosulphate and CCl_4 solutions, and makes the titration more rapid. Starch indicator could not be used in presence of alcohol, but the colour of the iodine itself was sufficient for titrations carried out in daylight.

Two early sets of results are shown in fig (4). Curves A and B show a slow initial rate of decomposition, then increased rate, and a slackening off as equilibrium is approached. This suggested two possibilities. 1) The I_2 liberated reacts with some impurity in the solvent, and the concentration of iodine does not rise rapidly until this impurity is used up. 2) The reaction is catalysed by its products, i.e. either by ethylene or by iodine.

In order to test the first possibility, five tubes, containing a solution of I_2 in the same CCl_4 as was used in the above experiments, were sealed up and heated at 100° C. They were opened and titrated at intervals of 24 hours. The initial titre of 10 c.c. was 7.2 c.c. N/100 thio. The tubes which had been heated from 1 to 5 days gave values 1) 7.2 2) 7.2 3) 7.1 4) 7.2 5) 7.15 c.c. There was therefore no appreciable action of I_2 on the solvent.

To/

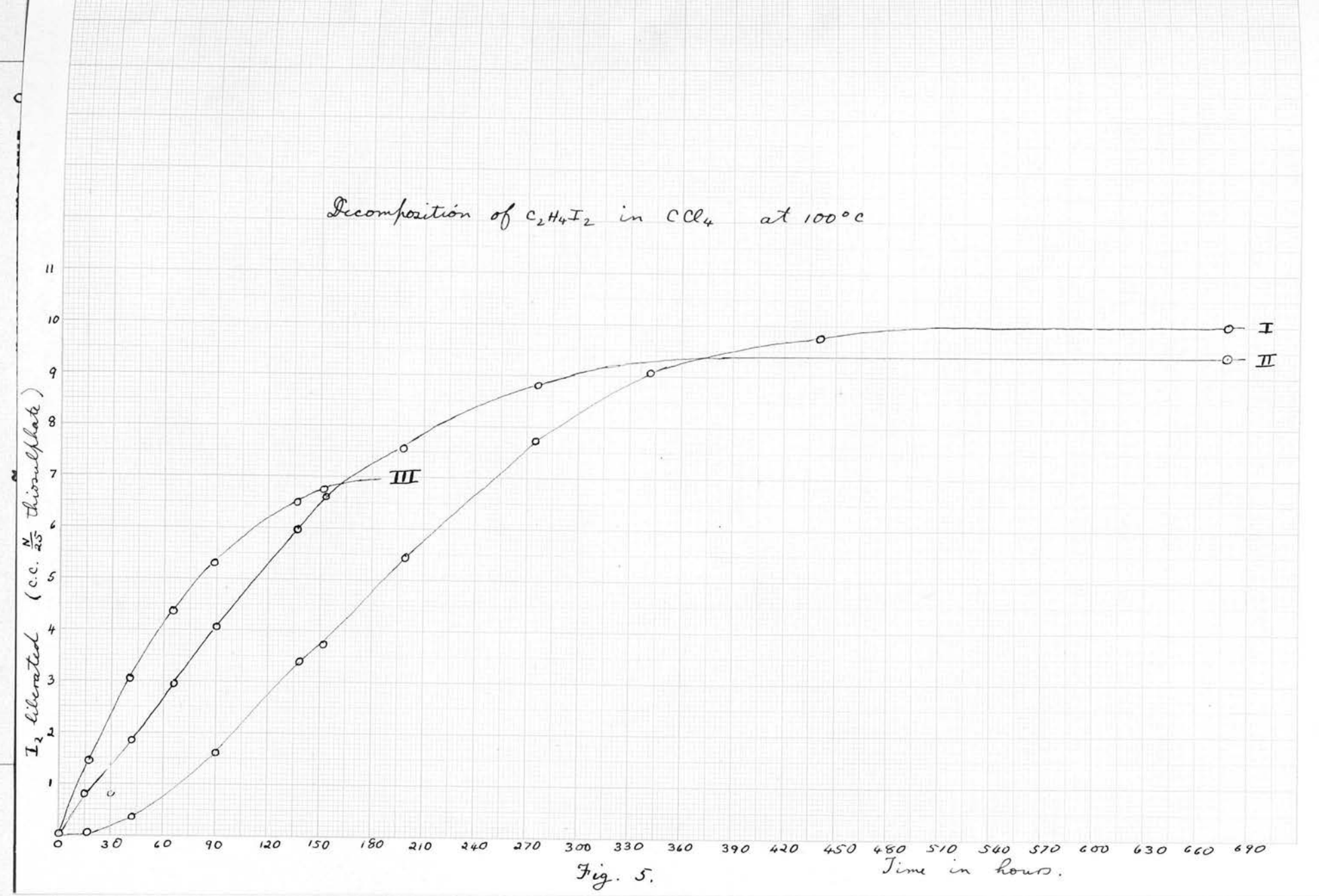

Decomposition of $C_2H_4I_2$ in CCl_4 at 100°C
I_2 liberated (c.c. $\frac{N}{25}$ thiosulphate)
Time in hours.
I
II
III
0
30
60
90
120
150
180
210
240
270
300
330
360
390
420
450
480
510
540
570
600
630
660
690
1
2
3
4
5
6
7
8
9
10
11

Fig. 5.

To test the second possibility, observations were made of the rate of decomposition of three different solutions, containing different initial concentrations of iodine. The tubes used were carefully made of the same volume in order that the ratio $\frac{C_2H_4 \text{ in liquid}}{\text{total } C_2H_4}$ should be constant. The results are given in fig.(5) and Table II.

Table II.

Solution I

$a = \cdot 04$ moles/litre ; $x_o < 10^{-5}$ moles/litre ; $f(x_o) = 7 \cdot 42$

Time t	x	$x - x_o$	mk
18.25 hrs	[.00006]	[.00005]	[0.84]
42.25	.00076	.00075	1.47
90	.00320	.00319	1.54
137.8	.00680	.00679	1.56
152.3	.00740	.00739	1.49
198.5	.01090	.01089	1.49
274.5	.01546	.01545	1.49
343	.01816	.01815	1.54
441	.01956	.01955	1.56
678	.02000	.01999	-

Solution II

$a = \cdot 04$ moles/litre ; $x_o = \cdot 004$ moles/litre ; $f(x_o) = 146 \cdot 1$

t	x	$x - x_o$	mk
18.5	.00560	.00160	1.81
41.75	.00780	.00380	1.64
66	.00990	.00590	1.86
90	.01220	.00820	1.56
137.5	.01600	.01200	1.54
152	.01730	.01330	1.59
199.25	.01924	.01524	1.51
276.25	.02164	.01764	1.58
678	.02280	.01880	-

Solution III

$a = \cdot 04$ moles/litre ; $x_o = \cdot 02$ moles/litre ; $f(x_o) = 255 \cdot 6$

t	x	$x - x_o$	mk
18	.02320	.00320	1.64
41.5	.02630	.00630	1.53
65.75	.02890	.00890	1.52
89.75	.03080	.0108	1.51
137	.03320	.0132	1.42
151.5	.03370	.0137	1.65

a = initial concentration of $C_2H_4I_2$.
x_o = initial concentration of I_2.

Curve I fig.(5) refers to a solution containing initially N/25 $C_2H_4I_2$, with a slight unavoidable I_2 coloration. The I_2 was estimated colorimetrically and found to be less than N/100,000. Cur ve II refers to a solution having initial concentrations of $C_2H_4I_2$ = N/25 and I_2 = N/250. Curve III refers to a solution having initial concentrations $C_2H_4I_2$ = N/25 and I_2 = N/50. Curve III is incomplete because several tubes of this solution burst in the water bath.

Curve I is of the same shape as curve B in fig.(4). Curve II shows increased initial rate of decomposition and in curve III the initial rate is still greater. Table III shows the relation between initial rate of decomposition and the I_2 concentration.

Table III.

Solution	$[I_2]$ initial	$\sqrt{[I_2]}$ initial	Initial Rate.
I	.0023	.048	.03
II	1	1	1
III	5	2.4	2

Allowing for the inaccuracy of reading the rates of decomposition from the curves of fig.(5), table III suggests that the rate of decomposition of $C_2H_4I_2$ in CCl_4 is proportional to $[I_2]^{\frac{1}{2}}$ and hence proportional to the concentration of iodine atoms. If this is so, the reverse action $C_2H_4 + I_2 \rightarrow C_2H_4I_2$ must also be catalysed by iodine atoms, because the equilibrium value/

value of $\frac{[C_2H_4][I_2]}{[C_2H_4I_2]}$ was found to be constant, viz. .02 mols/litre in solution I and .0198 mols/litre in solution II.

The course of the reaction should be represented by the following differential equation:-

$$\frac{d[C_2H_4I_2]}{dt} = k.[C_2H_4][I_2]^{3/2} - k'[C_2H_4I_2][I_2]^{1/2}$$

At equilibrium $0 = k[C_2H_4][I_2]^{3/2} - k'[C_2H_4I_2][I_2]^{1/2}$

$$\frac{[C_2H_4][I_2]}{[C_2H_4I_2]} = K$$

The actual value of $[C_2H_4]$ is less than the value deduced from the amount of $C_2H_4I_2$ decomposed, because a certain fraction of the C_2H_4 goes into the gas space above the liquid. If f is the ratio $\frac{[C_2H_4] \text{ in liquid}}{[C_2H_4] \text{ in gas}}$ at 100°C, the fraction of C_2H_4 in the liquid is $\underline{m} = \frac{fv_1}{fv_1 + v_2}$ where v_1 and v_2 are the volumes of liquid and gas respectively at 100°C. (In the above experiments v_1 = 12.4 c.c. v_2 = 5.6 c.c.).

This alters the differential equation to

$$\frac{d[C_2H_4I_2]}{dt} = k.m[C_2H_4][I_2]^{3/2} - k'[C_2H_4I_2][I_2]^{1/2}$$

and since $\frac{k'}{k} = \left(\frac{m[C_2H_4][I_2]}{[C_2H_4I_2]}\right)_{t=\infty} = mK \qquad k' = mkk$

so $$\frac{d[C_2H_4I_2]}{dt} = mk\left\{[C_2H_4][I_2] - k[C_2H_4I_2]\right\}[I_2]^{\frac{1}{2}} \quad ---(1)$$

where $[C_2H_4]$ and K are the values of the concentration of ethylene and of the equilibrium constant obtained by neglecting the loss of C_2H_4 from the solution.

On integration equation (1) gives

$$mk = \frac{1}{t} \cdot \frac{1}{\alpha+\gamma} \cdot 2\left\{f(x) - f(x_0)\right\} \quad ----(2)$$

where/

where $f(x) = \frac{2.303}{\alpha^{\frac{1}{2}}} \log_{10} \frac{\alpha^{\frac{1}{2}} + x^{\frac{1}{2}}}{\alpha^{\frac{1}{2}} - x^{\frac{1}{2}}} + \frac{2}{\gamma} \arctan \frac{x^{\frac{1}{2}}}{\gamma}$

$x = [I_2]$ at time t ; $x_0 = [I_2]$ at $t = 0$

$\alpha = \frac{B - \sqrt{B^2+4C}}{2}$; $\gamma^2 = -\frac{B - \sqrt{B^2+4C}}{2}$

$B = x_0 - k$; $C = K(a + x_0)$ $a = [C_2H_4I_2]$ at $t=0$

$K = .020$ moles/litre [from curves I & III fig.(5)]

Equation (2) was applied to the results of series I, II and III and sets of values of k were obtained which did not deviate greatly from a mean value of 1.54. These values are tabulated in Table II. The first value in series I is inaccurate because x was only determined very roughly by a colorimetric method. As the results cover a range of I_2 concentration from N/100,000 to N/30, they give a fairly strong confirmation of equation (1) as a correct representation of the course of the reaction.

Suggested mechanisms for the reaction involve the existence of a small amount of intermediate compound $C_2H_4I_3$ which can break down in two ways giving either ethylene di-iodide or ethylene.

$$C_2H_4I_2 + I \overset{(a)}{\rightleftharpoons} C_2H_4I_3 \overset{(b)}{\rightleftharpoons} C_2H_4 + I_3 \overset{(c)}{\rightleftharpoons} C_2H_4 + I_2 + I$$

To satisfy the conditions at equilibrium either (a) or (b) must be slow while the other reactions are instantaneous.

The reaction could also be explained by the following mechanism:-

$$C_2H_4I_2 + I \overset{(a)}{\rightleftharpoons} C_2H_4I + I_2 \overset{(b)}{\rightleftharpoons} C_2H_4 + I_2 + I$$

in/

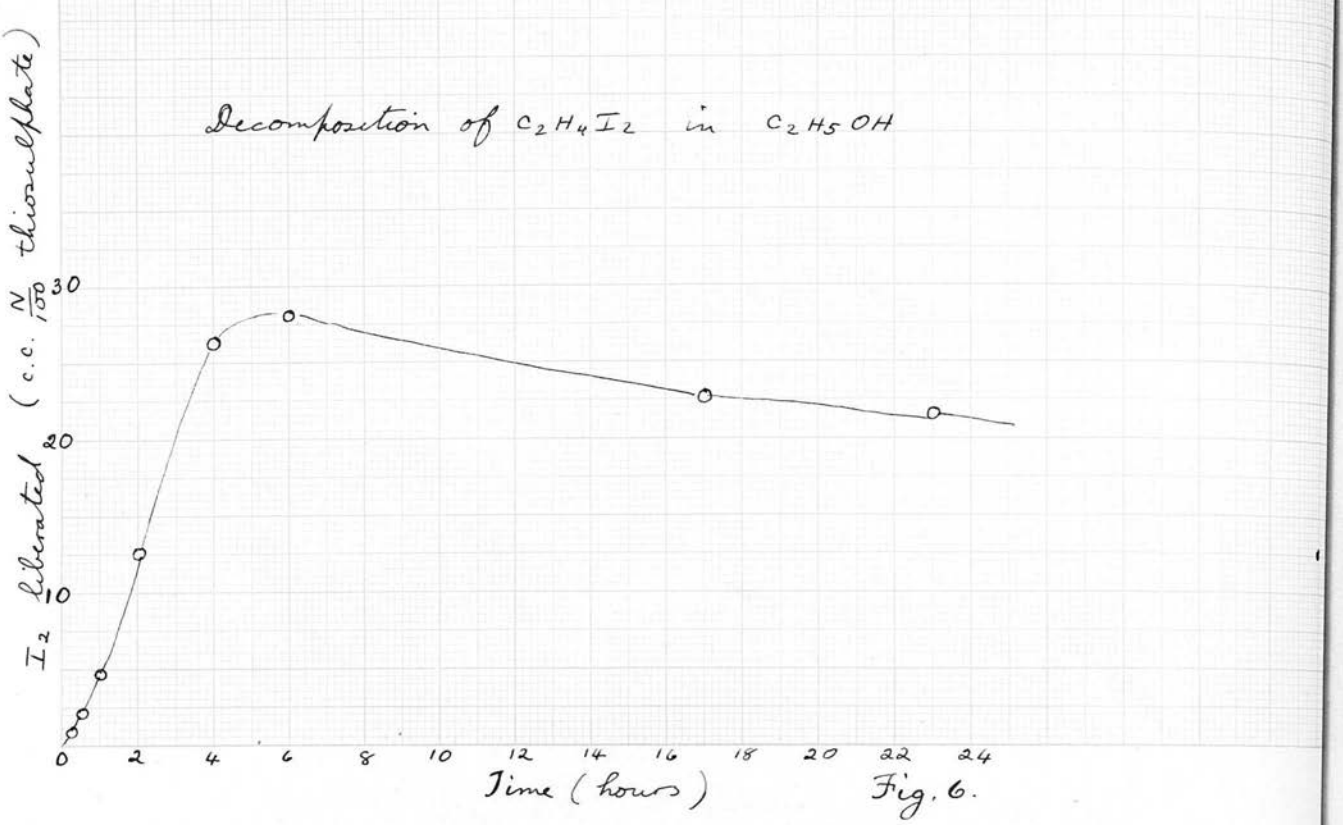

Decomposition of $C_2H_4I_2$ in C_2H_5OH
I_2 liberated (c.c. $\frac{N}{100}$ thiosulphate)
0
10
20
30
0
2
4
6
8
10
12
14
16
18
20
22
24
Time (hours)

Fig. 6.

in which either (a) or (b) is a slow reaction.

It is not possible to compare curves A and B (fig.(4)) with the curves of fig.(5), because the former were not carried to equilibrium, and also the relative volumes of liquid and air space were not measured in the case of curves A and B.

The value of $\underline{m}$ is not known because the solubility of ethylene in carbon tetrachloride at 100° C is not available. $\underline{m}$ and hence the solubility of ethylene, could be obtained by determining the equilibrium concentrations in tubes with a different ratio $\frac{\text{air}}{\text{liquid}}$. As such an experiment however, requires a time of 15 - 30 days for completion, it has not yet been carried out.

Decomposition of $C_2H_4I_2$ in alcohol.

The decomposition of $C_2H_4I_2$ in solution in C_2H_5OH is more complicated. The reaction is much more rapid, and there are subsidiary reactions. Fig.(6) shows the course of decomposition at 100° C of a solution containing initially 0.567 gm. $C_2H_4I_2$ in 100 c.c. The iodine concentration increases to a maximum and then decreases, indicating a reaction between iodine and the solvent C_2H_5OH.

There is also the possibility of a reaction between $C_2H_4I_2$ and C_2H_5OH. Baumstock (Ber., 7, 1172 and/

and 9 746) states that at 70°C there is a reaction

$$C_2H_4I_2 + C_2H_5OH \longrightarrow C_2H_4I.O.C_2H_5 + HI.$$

V. The dissociation pressure of ethylene di-iodide.

In order to calculate the equilibrium constant for the gas reaction $C_2H_4I_2 \rightleftharpoons C_2H_4 + I_2$ at a given temperature, it is necessary to know the concentration (or pressure) of gaseous I_2, $C_2H_4I_2$, and C_2H_4 in the equilibrium mixture.

The conditions of experiment ~~of~~ were chosen such that the pressures of iodine and ethylene di-iodide were always equal to their vapour pressures at the temperature in question. This was ensured by always having solid I_2 and $C_2H_4I_2$ present in the system.

If the vapour pressures of I_2 and $C_2H_4I_2$ are known, it only remains to measure the pressure of C_2H_4 in equilibrium with the two solids. The equilibrium constant K is then given by

$$K = \frac{(\text{Press. of } C_2H_4)\,(\text{Vap. press. of } I_2)}{(\text{Vap. press. of } C_2H_4I_2)}.$$

Vapour pressures of iodine were taken from the paper of Baxter, Hickey and Holmes (J.Amer.Chem. Soc., 29, 127).

The vapour pressure of ethylene di-iodide was measured as described in section VII.

The/

The "dissociation pressure" of ethylene di-iodide, i.e. the equilibrium pressure of ethylene, iodine and ethylene di-iodide above a mixture of solid iodine and solid ethylene di-iodide, was measured by means of a glass-spring manometer. This quantity, less the sum of the vapour pressures of iodine and ethylene di-iodide, gave $P_{C_2H_4}$, the equilibrium pressure of ethylene.

The apparatus used in measuring the dissociation pressure is shown in fig. (7).

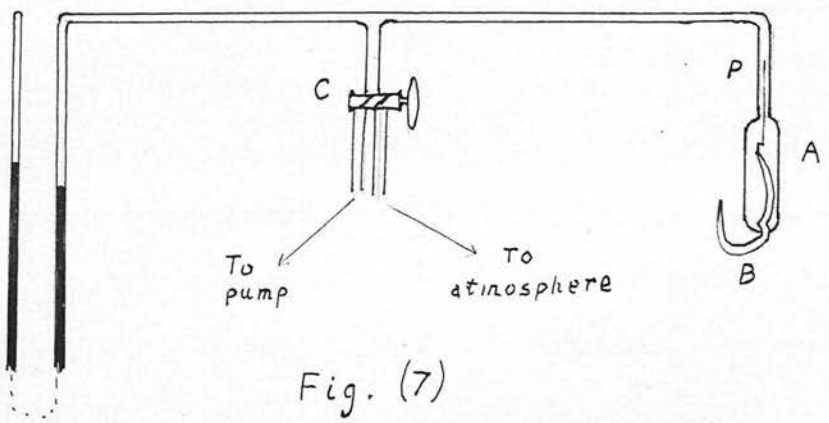


Fig. (7)

A is a glass spring manometer, consisting of a hollow curved glass spring with pointer attached, sealed into an outer glass jacket. Difference of pressure between the two compartments of the manometer causes the pointer P to move across the field of a microscope which is rigidly clamped to the manometer.

This type of manometer was used because manometric liquids such as oil, mercury, or sulphuric acid interact with ethylene or iodine.

The manometer was used as a zero instrument, i.e./

i.e., the pressure in the outer jacket of the manometer was adjusted until the pointer returned to the zero position. The pressure in the jacket was then equal to the pressure in the inner compartment of the manometer. Pressure regulation in the jacket was secured by means of the three-way tap C. connected to the pump and the atmosphere. With care the pressure could be adjusted to .1 mm. It was found best to adjust the pressure until the pointer was near the zero position but not necessarily exactly at zero. A correction was then applied to the pressure of the jacket, the correction being equal to the deviation from zero multiplied by the sensitivity of the manometer. Two different manometers were used, both of which had sensitivities of approximately 1 microscope scale division for a pressure difference of 1 millimetre of mercury.

It was found that the manometers were easily strained and had their zero shifted if the pressure difference was allowed to exceed about 5 centimetres of mercury.

The part of the jacket surrounding the pointer was made of narrow tubing so that a short focus microscope objective could be used. This obviated the necessity of making the manometer very sensitive and hence fragile.

The/

The arrangements for temperature regulation are shown in fig. (8).

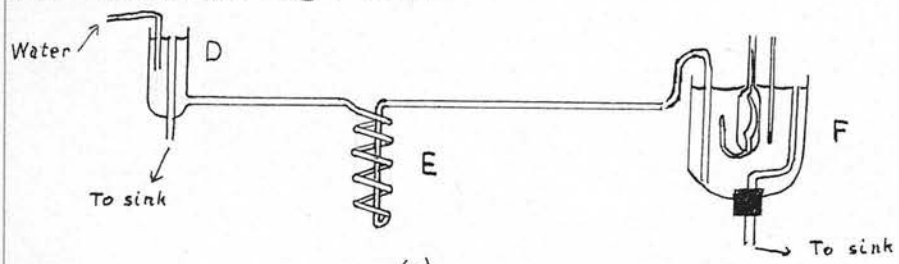


Fig. (8)

E is a spiral of glass tubing immersed in the vapour of boiling water or chloroform. F is the water bath surrounding the glass-spring manometer. The temperature of the bath F was altered by raising or lowering the constant level D, and hence increasing or decreasing the rate at which the water flowed through E. The tubing from E to F, and also the bath F itself, were well protected with cotton-wool.

This form of thermostat was not very satisfactory over long periods, but when it was watched pretty continuously it could be kept constant to about .2°C. Its advantages were that no heating or control arrangements were near the manometer and microscope, and so there was no risk of disturbing the setting.

The glass-spring manometer was cleaned before use with chromic acid, washed with distilled water, and dried in a steam oven. A small quantity (0.1 to 0.2 gm.) of $C_2H_4I_2$, purified as in section II, was introduced into the bent tube B. The inner and outer compartments/

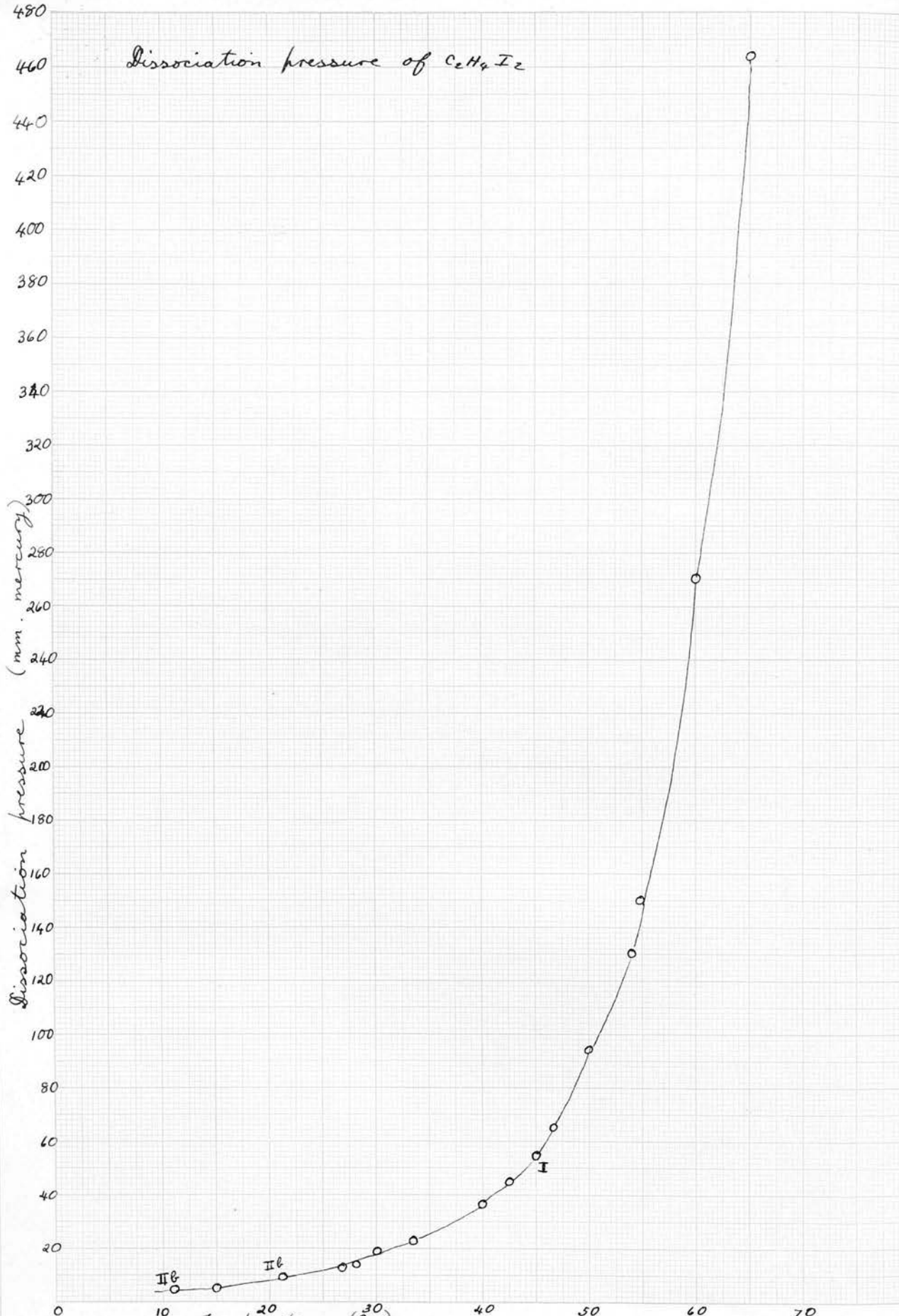

Dissociation pressure of $C_2H_4I_2$
480
460
440
420
400
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
Dissociation pressure (mm. mercury)
10
20
30
40
50
60
70
Temperature (°C)
IIb'
IIb
I

Fig. (9)

compartments of the manometer were simultaneously evacuated with a Hyvac oil pump for 15 - 30 minutes in order to remove traces of moisture and CCl_4. The zero position of the pointer P was read at this time, when there was no% pressure difference between the two parts of the manometer. The bent tube B was then sealed off with a hand blow-pipe, and the thermostat was raised into position arouend the manometer. Light was excluded from the thermostat by screens of cotton-wool and asbestos board.

The thermostat was kept at one temperature for several days till the pressure in the manometer reached a steady value. Then the temperature was changed and another equilibrium pressure obtained.

Only one equilibrium pressure (at 45°C) was measured with manometer I, which was broken by an accidental increase of pressure in the outer jacket. (Manometers such as these could stand a pressure difference up to about 20 cm. of mercury).

With manometer II several equilibrium pressures were measured over a period of 7 - 8 weeks.

Two readings were taken with manometer II after refilling it with $C_2H_4I_2$ to which a little resublimed I_2 had been added, and after washing out the residual air with ethylene gas before evacuating.

The three sets of results, which are given in Table IV and fig.(9), show good agreement.

Table IV/

Table IV.

Manometer	Temp.	Press.	Manometer	Temp.	Press.
II (b)	11°C	4.3mm	II (a)	42.6°C	45.0 mm.
II (a)	15	5.0	I	45.0	54.2
II (b)	21.5	9.0	II (a)	46.7	65.0
II (a)	26.8	12.5	"	50.0	94.5
"	28.2	13.9	"	53.4	131.4
"	30.0	18.8	"	54.9	150
"	33.4	22.4	"	60.0	275
"	40.0	36.6	"	65.0	464

VI Kinetics of the formation of ethylene di-iodide.

An attempt was made to obtain values of the velocity constant $\underline{k}'$ of the reaction between C_2H_4 and I_2 in the gaseous state, by assuming the rate of change of pressure in the glass-spring manometers of section V to be given by

$$\frac{dP}{dt} = k \cdot P_{C_2H_4I_2} - k' \cdot P_{C_2H_4} \cdot P_{I_2} \quad \cdots (1)$$

where $P_{C_2H_4I_2}$ and P_{I_2}, the vapour pressures of $C_2H_4I_2$ and I_2 are constants. On integration this gives

$$k' = \frac{2.303}{t} \cdot \frac{1}{P_{I_2}} \cdot \log_{10} \frac{P_\infty - P_0}{P_\infty - P} \quad \cdots (2)$$

where P_∞ is the equilibrium pressure, P_0 the pressure at time $\underline{t} = 0$ and P the pressure at time $\underline{t}$.

Equation (2) was applied to some of the experimental values of P. The values of $\underline{k}'$ thus obtained were approximately constant for single sets of/

of readings, provided they were not spread over more than a few hours, but over longer periods a steady "drift" in the value of k' was observed. k' also depended on the previous history of the system, e.g., the temperature to which it had previously been heated, which affected the amount of adsorbed C_2H_4. In some cases, when the manometer was suddenly cooled, the pressure (initially greater than P_∞ for the lower temperature) dropped to a value below P_∞ and then rose gradually to P_∞. This initial decrease was much too great to be explained by contraction of the gas on cooling, and must be ascribed to the increased amount of C_2H_4 adsorbed at the lower temperature.

k', though not a true constant, was always of the order of 10^{-3} $mm.^{-1}$ $min.^{-1}$ at temperatures from 20°C to 45°C, thus showing a remarkably low temperature coefficient. If, however the term $\frac{1}{P_{I_2}}$ is removed from equation (2), the values of k' would show the usual exponential increase with temperature. This indicates that the reaction assumed in the theoretical deduction of k' is not followed in reality. The combination of C_2H_4 and I_2 probably takes place on walls of the vessel, or on the surface of I_2 or $C_2H_4I_2$, and not in the body of the gas as was postulated above.

If the reaction is a surface reaction it resembles/

resembles the reactions between ethylene and chlorine or bromine which seem to take place entirely on the walls of the containing vessel. (Stewart and Edlund, J.Amer.Chem.Soc.,45,1014; Norrish,J.C.S.(1923)3006; Norrish and Jones,J.C.S.,(1926) 55; Stewart and Fowler, J.Amer.Chem.Soc.,48 1187).

A set of observations of P and the corresponding values of k' at 26.8°C are given in table V, and the values of k'obtained at various temperatures are given in table VI.

Table V.

At 26.8°C P_{I_2} = 0.4 mm. and P_∞ = 12.5 mm.

t min.	P mm.	k'
0	0.9	-
60	1.2	1.22 x 10^{-3}
255	2.5	1.6 "
300	3.1	2.0 "
360	3.8	2.2 "
1152	9.0	2.8 "
1212	9.6	3.1 "
1800	11.7	4.0 "
∞	12.5	-

Table VI.

Temperature	k'
15°	7.8 x 10^{-3}
26.8	1.2 - 4.0 x 10^{-3}
27.5	5.7 x 10^{-3}
31	8.2 "
38	9.7 "
45	4.3 "
46.5	4.7 "

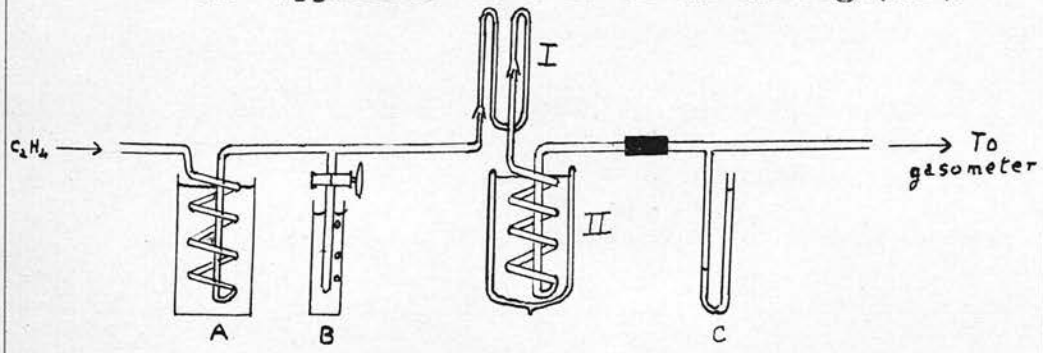
VII. The vapour pressure of ethylene di-iodide.

A knowledge of the vapour pressure of ethylene di-iodide was necessary in order to complete the results of section V.

Static methods of measuring the vapour pressure of $C_2H_4I_2$ are unsuitable, both on account of of its tendency to decompcsition and because of the low value of its vapour pressure at the temperatures in question.

A gas-stream method was decided upon, such as had been used by Pfaudler (Ann.der Phys. 63,36) to determine the vapour pressure of mercury, and by Baxter, Hickey and Holmes (J.Amer.Chem.Soc.,29,127) to determine the vapour pressure of iodine. The method consists essentially in saturating a large volume of gas with the vapour of the substance under investigation, and measuring the loss of weight of the substance. In order to prevent decomposition of the $C_2H_4I_2$, ethylene at atmospheric pressure was chosen as the gas to be saturated.

The apparatus used is shown in fig.(10).



Tube/ Fig. (10)

Tube I (40 cm. long) contained a layer of solid ethylene di-iodide, held in place by means of glass wool. It was kept at a constant temperature by a copper air bath with a vapour jacket which was filled with boiling ether, carbon disulphide, or acetone. Tube I was connected by an ungreased ground joint to tube II, a spiral cooled with ether and solid CO_2. The joint between tubes I and II was kept well within the air bath. Any leakage at the joint could be readily detected by difference in pressure at B and C.

A stream of dried ethylene from a cylinder of compressed gas was passed through the spiral A, where it was heated approximately to the temperature of tube I, and then through tubes I and II. The escape at B kept the pressure of ethylene constant.

The vaporised $C_2H_4I_2$ was condensed in tube II. The volume of ethylene which passed through was determined by collecting in a calibrated gasometer, the water in which was previously saturated with ethylene.

Tubes I and II were weighed before and after each experiment. Tube II was washed externally with pure ether before weighing. The loss of weight of tube I and gain of weight in tube II usually agreed to 1 milligram.

The temperature of the air bath was taken ten or twelve times during each experiment, and the mean/

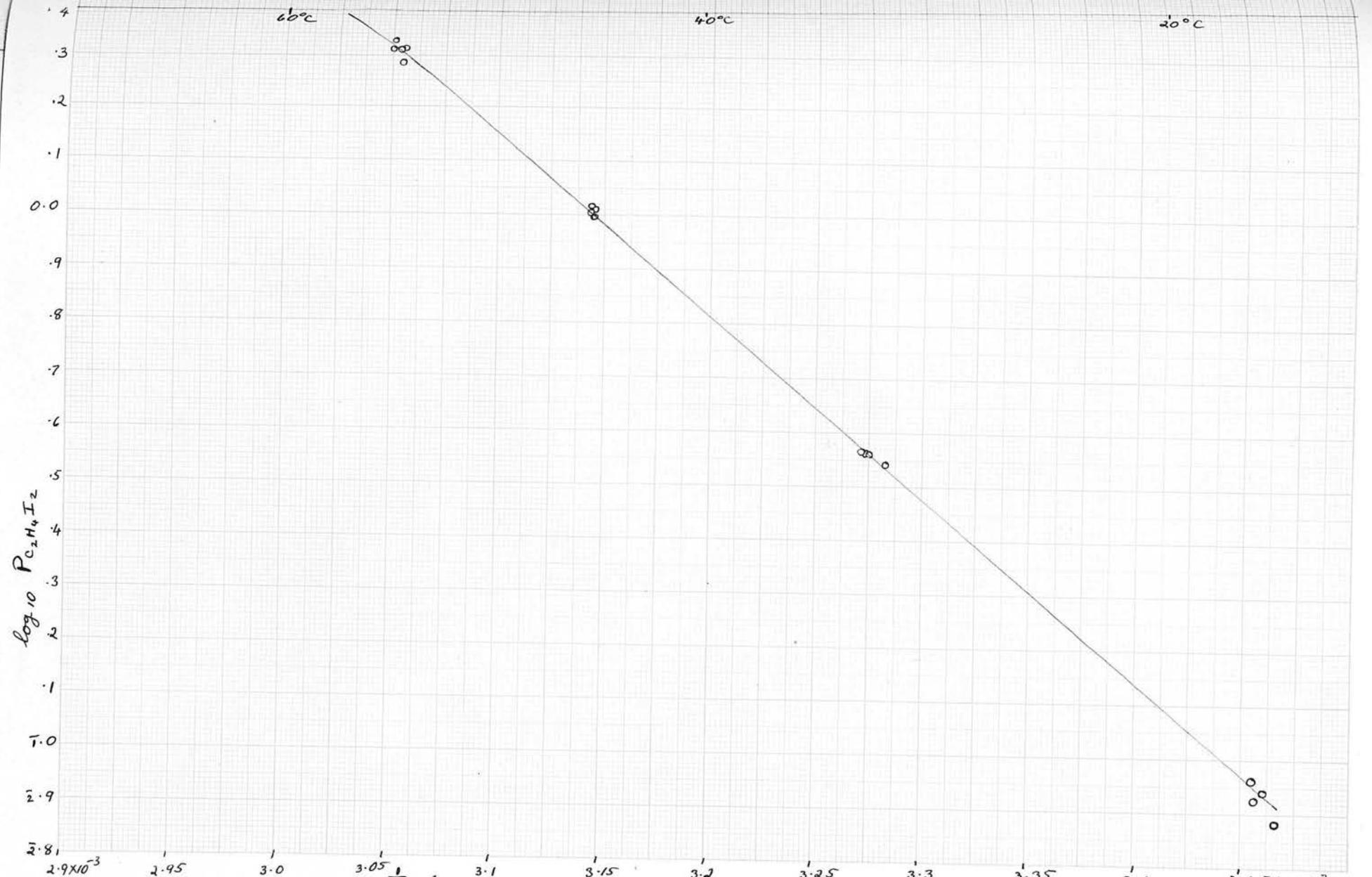

60°C
40°C
20°C
log10 $P_{C_2H_4I_2}$
·4
·3
·2
·1
0·0
·9
·8
·7
·6
·5
·4
·3
·2
·1
1·0
1·9
2·8
2·9×10⁻³
2·95
3·0
3·05
3·1
3·15
3·2
3·25
3·3
3·35
3·4
3·45 × 10⁻³
1/T° abs.

Fig. 11.

mean value was taken as the temperature of tube I.

The weight of $C_2H_4I_2$ vaporised varied from .008 gm. at room temperature to 0.15 gm. at 55°C. The time occupied by a run varied from 30 to 75 minutes, and the volume of ethylene collected from 3000 to 6000 c.c.

At 55°C the $C_2H_4I_2$ which collected in tube II showed distinct iodine coloration, so the experiments were not extended to higher temperatures.

Calculation of the vapour pressure.

If x gm = weight of $C_2H_4I_2$ vaporised

V c.c. = volume of gas in gasometer at t_1°C under a pressure of p_1 mm. (p_1 being corrected for the vapour pressure of water at t_1°C);

p_2 mm. = pressure of ethylene in tube I (= the mean pressures at B and C),

then the vapour pressure of $C_2H_4I_2$

$$P_{C_2H_4I_2} = \frac{22400}{V} \times \frac{760 \times p_2}{p_1} \times \frac{273 + t_1}{273} \times \frac{x}{281.9}$$

281.9 being the molecular weight of $C_2H_4I_2$.

The results are given in table VII.

In fig.(11) $\log_{10} P_{C_2H_4I_2}$ is plotted against the reciprocal of the absolute temperature. It is a satisfactory straight line.

From fig.(11) the molecular latent heat of sublimation of $C_2H_4I_2$

$$L = 2.303 \times R \times \frac{d(\log_{10} P_{C_2H_4I_2})}{d(1/T)} = 2.303 \times 1.985 \times 3.43 \times 10^3$$

$$= 15700 \text{ cal.}$$

Table VII.

Temperature of air-bath	V	Loss of weight Tube I	Gain of weight Tube II	Mean Change of I & II	$P_{C_2H_4I_2}$
16.2°C	5630c.c.	.0077gm.	.0075gm.	.0076gm.	0.084 mm.
16.4	5600	.0081	.0081	.0081	0.091
15.3	5670	.0066	.0071	.0069	0.076
15.9	5670	.0077	.0081	.0079	0.087
31.6	5030	.0278	.0271	.0275	0.350
32.3	5320	.0311	.0302	.0307	0.362
32.5	5390	.0321	.0310	.0316	0.367
32.6	5000	.0295	.0289	.0292	0.369
45.0	4390	.0724	.0713	.0719	1.029
45.0	5180	.0821	.0810	.0815	0.987
45.1	4520	.0753	.0743	.0748	1.043
45.1	5500	.0894	.0886	.0890	1.021
54.4	3050	.0928	.0923	.0926	1.92
54.4	4760	.1565	.1567	.1566	2.07
54.5	3180	.1041	.1030	.1036	2.06
54.8	3090	.1053	.1046	.1050	2.15
54.9	3990	.1316	.1308	.1312	2.08

VIII Equilibrium constants of the reaction:

$$C_2H_4 + I_2 \rightleftharpoons C_2H_4I_2$$

From the results of sections V and VII it is possible to calculate equilibrium constants for the reaction

$$C_2H_4 + I_2 \rightleftharpoons C_2H_4I_2$$

The equilibrium constant K is given by the expression

$$K = \frac{[C_2H_4][I_2]}{[C_2H_4I_2]}$$

$[I_2]$ and $[C_2H_4I_2]$ are put equal to the vapour pressures of I_2 and $C_2H_4I_2$ respectively.

$[C_2H_4]$ is equal to the dissociation pressure P given in section V, less the sum of the vapour pressures/

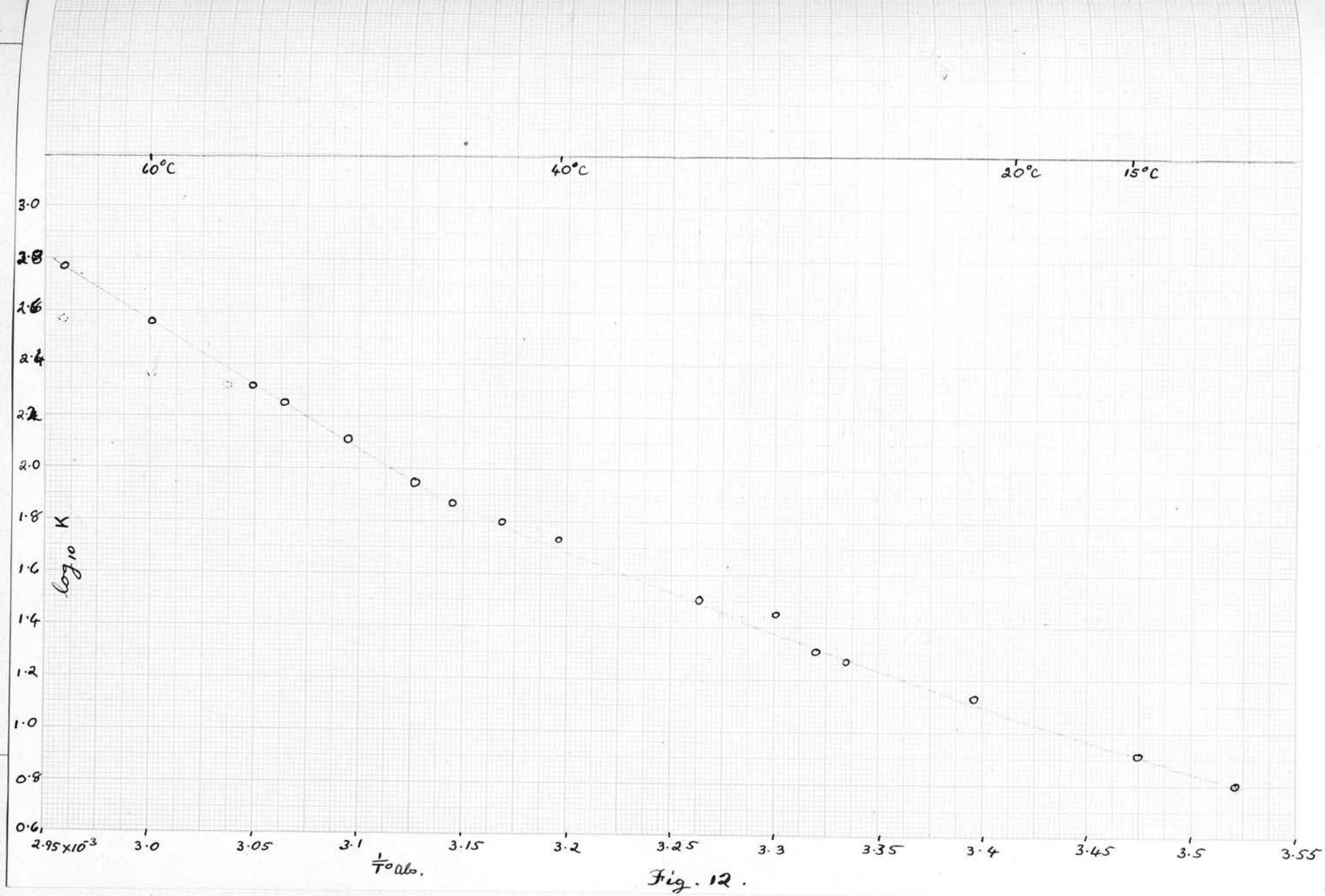

60°C
40°C
20°C
15°C
3·0
2·8
2·6
2·4
2·2
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
log10 K
2·95×10⁻³
3·0
3·05
3·1
3·15
3·2
3·25
3·3
3·35
3·4
3·45
3·5
3·55
1/T° abs.

Fig. 12.

pressures of I_2 and $C_2H_4I_2$.

Values of P_{I_2}, the vapour pressure of I_2, were taken from the results of Baxter, Hickey and Holmes (J.Amer.Chem.Soc., 29, 127).

Values of $P_{C_2H_4I_2}$ were read from fig.(11). It was necessary to extrapolate to get values for $P_{C_2H_4I_2}$ at 60° and 65°, but the straight line nature of the curve made extrapolation justifiable.

The results are given in table VIII.

When K is plotted against the temperature it gives a smooth curve of the same appearance as fig. (9). In fig. (12) $\log_{10} K$ is plotted against the reciprocal of the absolute temperature. The resulting curve deviates distinctly from the expected straight line. There is a suggestion of a sudden change of slope at 40° - 45°C.

Table VIII./

Table VIII.

Temperature	P	$P_{C_2H_4I_2}$	P_{I_2}	$P_{C_2H_4}$	K
11.0°C	4.3mm.	0.056mm.	0.086mm.	4.1mm.	6.3 mm.
15.0	5.0	0.077	0.131	4.8	8.1
21.5	9.0	0.141	0.224	8.6	13.7
26.8	12.5	0.227	0.355	11.9	18.6
28.2	13.9	0.255	0.394	13.3	20.5
30.0	18.8	0.299	0.469	18.0	28.3
33.4	22.4	0.400	0.603	21.4	32.4
40.0	36.6	0.675	1.025	34.9	53.1
42.6	45.0	0.836	1.23	42.9	63.2
45.0	54.2	1.02	1.50	51.7	75.6
46.7	65.0	1.18	1.73	62.1	90.6
50.0	94.5	1.51	2.15	90.8	129
53.4	131.4	1.93	2.69	126.8	177
54.9	150	2.14	3.97	145	208
60.0	275	3.14	4.29	268	365
65.0	464	4.52	5.96	453	597

It is of interest that Kurbatow (Z.f.anorg. Chem.56,230) states that the two forms of iodine described by Fedorow (Bull.Acad.Sci.St.Peterbourg 22 287) have a transition temperature at 46°- 47°C. It was thought that the difference in vapour pressure of the two forms of iodine might account for the change of slope in fig.(12). The change of slope is however, too great to be explained in this way. The heat of formation H of gaseous $C_2H_4I_2$ from gaseous I_2 and C_2H_4 was calculated from the slope of the curve in fig.(12) by the equation

$$H = 2.303 \times R \times \frac{d \log_{10} K}{d(1/T)}$$

H/

H was found to be 22300 calories per gram molecule at 50° C and 13400 calories at 30° C. The difference, 8900 calories, is much too great for the heat of transformation of two crystalline forms of iodine.

The value obtained for H at 50° is in good agreement with the value calculated from thermochemical data. Berthelot's value for the molecular heat of combustion of $C_2H_4I_2$ at constant pressure is 324800 calories (Ann. Chim. Phys. 21, 296). Mixter's value for the molecular heat of combustion of ethylene at constant pressure is 345,800 calories. The molecular heats of sublimation of I_2 (Baxter, Hickey and Holmes, J. Amer. Chem. Soc. 29. 127) and $C_2H_4I_2$ (Section VII) are 15100 and 15700 calories respectively. Hence the heat of for mation of gaseous ethylene di-iodide from ethylene and gaseous iodine is 345800 - 324800 - 15700 + 15100 = 20,400 calories per gram molecule, compared with the value 22300 calories obtained from the high te mperature part of fig.(12).

Two further possibilities suggest themselves as explanations of the deviation from a straight line in fig.(12)

(1) The vapour pressure of ethylene di-iodide is increased at higher temperatures by a "solubility" effect in the increased pressure of ethylene.

(2) The vapour pressure of iodine is lowered at the/

the low temperatures by adsorbed C_2H_4 or $C_2H_4I_2$ in solid solution.

(1) would imply that it is the high temperature part of the curve that is at fault. This is improbable because the points from 40° to 65° C lie very closely on a straight line. Deviations are more marked below 40° . The pressure of ethylene is also very small (1/20 to 1/2 atmosphere) and an effect of this kind seems improbable, although it is known that at a pressure of 300 atmospheres ethylene gas dissolves ethylene di-iodide and iodine to a marked extent. (Villard, Chem. News 1898, 297)

(2) seems a fairly probable explanation.

Other explanations, such as increased solubility of iodine in ethylene, or reduction of the vapour pressure of ethylene di-iodide would give a change of slope in the wrong direction.

If (2) is the correct explanation, the values of K given in table VIII will be too great at temperatures much below 40° C.

IX Summary.

The rates of formation and decomposition of ethylene di-iodide in the gaseous state have been studied (sections III and VI). The results obtained indicate that these reactions are not homogeneous but take place on the walls of the reaction vessel or/

or on the surface of the solid reactants.

The rates of formation and decomposition in solution in carbon tetrachloride at 100°C were found to be proportional to the square root of the iodine concentration. Suggested mechanisms are put forward to explain this reaction (section IV).

The dissociation pressure of ethylene di-iodide has been measured at several temperatures. By combining these measurements with measurements of the vapour pressure of iodine and ethylene di-iodide, equilibrium constants of the reaction have been obtained.

(b) (2)

.—The Thermal Equilibrium between Ethylene, Iodine, and Ethylene Di-iodide. By R. B. Mooney, M.A., B.Sc., and E. B. Ludlam, M.A., D.Sc.

(MS. received December 8, 1928. Read January 21, 1929.)

Object of Work.

This work was undertaken in order to study the thermal and photochemical reaction between ethylene and iodine, which preliminary experiments had shown to give some promise of furnishing useful data in connection with the modern study of homogeneous gas reactions.

The present paper deals with the reaction in the absence of light. The reaction proved to be non-homogeneous under the conditions actually realised. This is not in itself surprising, as many reactions which at one time were regarded as homogeneous have turned out on more critical study to be non-homogeneous.

The values obtained for the equilibrium constants are of interest in themselves, and will prove of use as a starting-point for further investigations in which the displacement of the equilibrium by light will be studied.

I. Preparation of Ethylene Di-iodide.

Ethylene di-iodide $C_2H_4I_2$ was prepared by Semenow's method (*Jahresbericht über die Fortschritte der Chemie*, 1864, 483), viz. by passing ethylene into iodine crystals covered with absolute alcohol. The resulting ethylene di-iodide was washed with a little alcohol, dried, and recrystallised from carbon tetrachloride. The crystals thus obtained keep colourless if left exposed to the air, because the iodine which is produced by decomposition volatilises as soon as formed. In a desiccator or other confined space small crystals of iodine gradually appear among the ethylene di-iodide crystals. If alcoholic impurity is present, the crystals rapidly turn brown. The best way of keeping ethylene di-iodide was found to be to seal it up in an atmosphere of ethylene. Samples have been kept in this way for five months without decomposition.

The pure crystals melted at 81° C.

II. Measurements of the Dissociation Pressure of Ethylene Di-iodide.

To measure the "dissociation pressure" of ethylene di-iodide, *i.e.* the total pressure of gaseous ethylene, iodine, and ethylene di-iodide in equilibrium with solid ethylene di-iodide and solid iodine, it is necessary to use a manometer which does not absorb ethylene or iodine. Manometric liquids, such as mercury, sulphuric acid, or oil, cannot be used. Several glass spring manometers (as shown in fig. 1) were therefore made. The outer jacket of the manometer was connected to a mercury manometer and to a three-way tap for regulating the pressure in the jacket. The

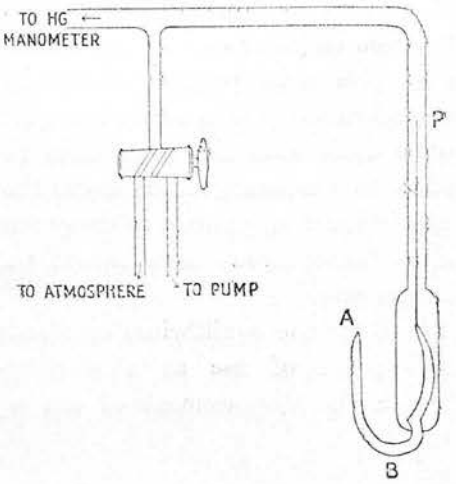


Fig. 1.

pointer P was observed with a microscope, and was kept at its zero position by adjusting the pressure in the jacket. The sensitivity of the manometers was approximately one microscope scale-division per millimetre of mercury, so that the pressure could be estimated to ·1 mm.

A small quantity (0·1 to 0·2 gm.) of ethylene di-iodide was introduced into the bent tube B at the bottom of the manometer. The inner and outer compartments were simultaneously evacuated with a motor-driven oil pump for fifteen minutes, and then the bent tube was sealed off at A. During evacuation, when there was no pressure difference between the two compartments of the manometer, the zero position of the pointer P was noted.

A small thermostat was then placed in position round the manometer, which was shielded from direct light.

The thermostat was kept at one temperature for several days till the pressure reached an equilibrium value. Then the temperature was

changed and another equilibrium pressure obtained. In this way a series of pressures between 15° and 65° was obtained.

Only one equilibrium pressure reading (at 45°) was obtained with manometer I, which was broken by an accidental increase of pressure in the outer jacket. Manometer II gave several readings over a period of seven to eight weeks. One or two readings taken with manometer II after refilling with ethylene di-iodide, to which a little resublimed iodine was added, are in agreement with the previous readings. The results are given in Table I.

TABLE I.

Temp.	Pressure.	Temp.	Pressure.
	mm.		mm.
11°	4·3	40·0	36·6
15	5·0	42·6	45·0
21·5	9·0	45	54·2
26·8	12·5	46·7	65·0
28·2	13·9	50·0	94·5
30·0	18·8	53·4	131·4
33·4	22·4	54·9	150
		60·0	275
		65	464

III. Vapour Pressure of Ethylene Di-iodide by the Gas-stream Method.

In order to measure the pressure of undissociated ethylene di-iodide vapour in equilibrium with the solid, a dynamic method was used. The apparatus is shown diagrammatically in fig. 2.

Tube I (40 cm. long) contained a layer of solid ethylene di-iodide. It was kept at a constant temperature by a copper air-bath with vapour jacket, which was filled with boiling ether, carbon disulphide, or acetone. Tube I was connected by an ungreased ground joint to tube II, a spiral cooled with ether and solid CO_2. Any leakage at the joint could be readily detected by difference in pressure at B and C. A stream of dried ethylene from a cylinder of compressed gas was passed through the spiral A, where it was heated approximately to the temperature of tube I, and then through tubes I and II. The escape at B kept the pressure of ethylene constant. The gas was saturated with ethylene di-iodide in passing through tube I, dissociation of the di-iodide being checked by the high pressure of ethylene.

The ethylene di-iodide vaporised was condensed in tube II. The volume of ethylene which passed through was determined by collecting

in a calibrated gasometer, the water in which was previously saturated with ethylene.

Tubes I and II were weighed before and after each experiment. The loss of weight of I and gain of weight of II usually agreed to 1 milligram.

The weight of ethylene di-iodide vaporised varied from 0·008 gm. at room temperature to 0·15 gm. at 55° C. The time occupied by a run

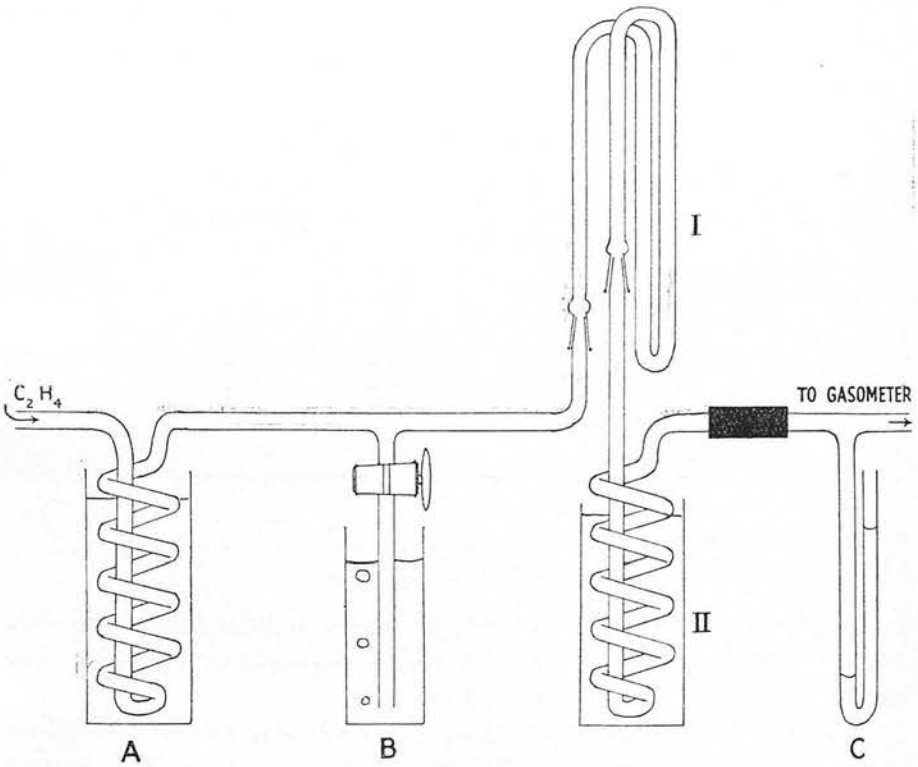


FIG. 2.

varied from thirty to seventy-five minutes, and the volume of gas collected from 3000 to 6000 c.c.

At 55° the di-iodide which collected in II showed distinct iodine coloration, so the experiments were not extended to higher temperatures.

Calculation of Vapour Pressure of Ethylene Di-iodide.

Let x gm. = weight of $C_2H_4I_2$ vaporised,

V c.c. = volume of gas in gasometer at temperature t_1° C. and pressure p_1 mm. (p_1 being corrected for the vapour pressure of water at t_1° C.),

p_2 mm. = pressure of C_2H_4 in tube I (= average of pressures at B and C).

Then the vapour pressure $P_{C_2H_4I_2}$

$$= \frac{22400}{V} \times \frac{760 \times p_2}{p_1} \times \frac{273 + t_1}{273} \times \frac{x}{281{\cdot}9} \text{ mm.}$$

where 281·9 is the molecular weight of ethylene di-iodide.

The results are shown in Table II.

TABLE II.

Temp.	Pressure.	Temp.	Pressure.
°C.	mm.	°C.	mm.
16·2	0·084	45·0	1·03
16·4	0·091	45·0	0·99
15·3	0·076	45·1	1·04
15·9	0·087	45·1	1·02
31·6	0·350	54·4	1·92
32·3	0·352	54·4	2·07
32·5	0·367	54·5	2·06
32·6	0·369	54·8	2·15
		54·9	2·08

The logarithmic vapour pressure curve (fig. 3), is a satisfactory straight line. From the slope of the curve the molecular latent heat of sublimation was found to be 15,700 calories.

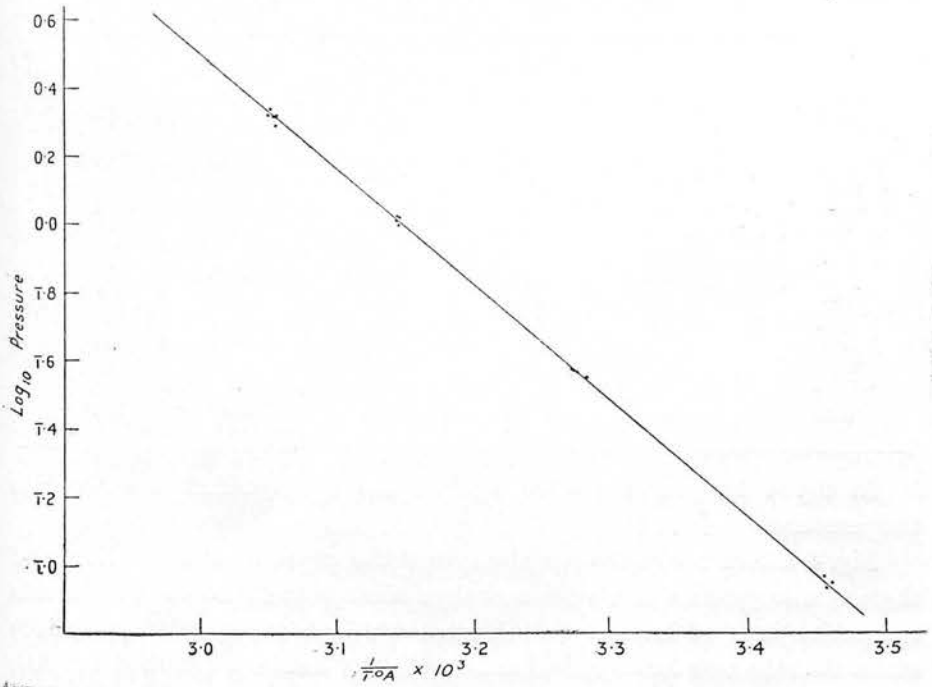


FIG. 3.

IV. Equilibrium Constants of the Reaction $C_2H_4 + I_2 \rightleftharpoons C_2H_4I_2$.

From the results given in sections II. and III. it is possible to calculate equilibrium constants of the reaction $C_2H_4 + I_2 \rightleftharpoons C_2H_4I_2$,

$$K = \frac{[C_2H_4][I_2]}{[C_2H_4]}.$$

$[I_2]$ and $[C_2H_4I_2]$ are equal to the vapour pressures of iodine and ethylene di-iodide respectively.

$[C_2H_4]$ is equal to the dissociation pressure given in section II., less the vapour pressures of iodine and ethylene di-iodide.

Values of P_{I_2}, the vapour pressure of iodine, were taken from the results of Baxter, Hickey, and Holmes (*J.A.C.S.*, **29**, 127). Values of $P_{C_2H_4I_2}$ were read from fig. 3. It was necessary to extrapolate to get $P_{C_2H_4I_2}$ at 60° and 65° C. The results are given in Table III.

Table III.

Temperature. °C.	Dissociation Pressure. P mm.	$P_{C_2H_4I_2}$. a mm.	P_{I_2}. b mm.	$P_{C_2H_4}$. c mm.	K. $\frac{c \cdot b}{a}$
11	4·3	·056	·086	4·1	6·31
15	5·0	·077	·131	4·8	8·13
21·5	9·0	·141	·224	8·6	13·7
26·8	12·5	·227	·355	11·9	18·6
28 2	13·9	·255	·394	13 3	20·5
30·0	18·8	·299	·469	18·0	28·3
33·4	22·4	·400	·603	21·4	32·4
40·0	36·6	·675	1·025	34·9	53·1
42·6	45·0	·836	1·23	42·9	63·2
45	54·2	1·02	1·50	51·7	75·6
46·7	65·0	1·18	1·73	62·1	90·6
50·0	94·5	1·51	2·15	90·8	129
53·4	131·4	1·93	2·69	126·8	177
54·9	150	2·14	3·07	145	208
60·0	275	3·14	4·29	268	365
65·0	464	4·52	5·96	453	597

In fig. 4 $\log_{10} K$ is plotted against the reciprocal of the absolute temperature.

Fig. 4 shows a distinct deviation from the expected straight line, and there is a suggestion of a sudden change of slope at 40° to 45° C. In this connection it is of interest that Kurbatow (*Z. f. anorg. Chem.*, **56**, 230) states that the two forms of iodine described by Fedorow (*Bull. Acad. Sci. de St Petersbourg*, **22**, 287) have a transition temperature at 46° to 47° C.

The difference in the vapour pressures of the two forms might account for the change of slope in fig. 4.

An alternative explanation might be found in the possibility of the occurrence of solid solutions of one or other form of iodine in ethylene di-iodide and consequent lowering of the vapour pressure of ethylene di-iodide.

lowering the vapour pressure of iodine at low temperatures by ethylene or ethylene di-iodide adsorbed on the surface of the solid iodine.

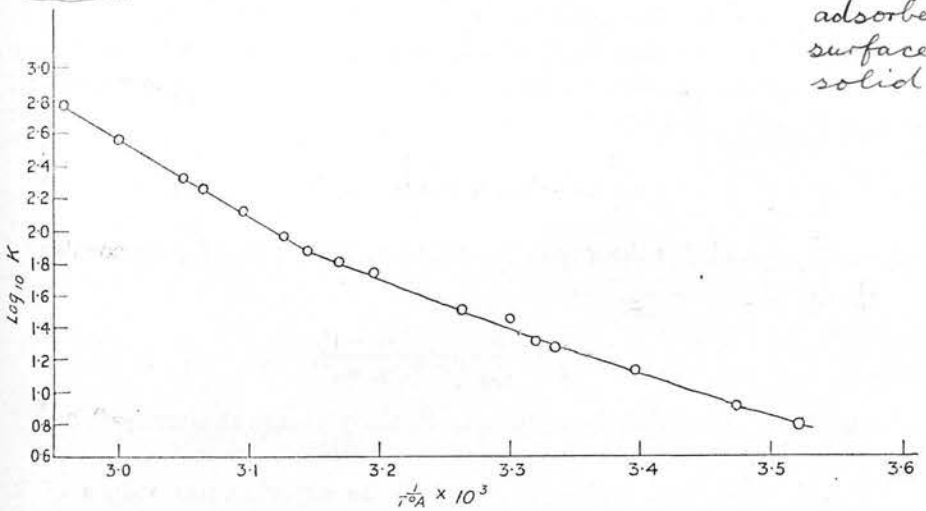


FIG. 4.

The heat of formation of gaseous ethylene di-iodide from ethylene and gaseous iodine was calculated from fig. 4 by using the equation

$$\frac{H}{R} = \frac{d(\log_e K)}{d\left(\frac{1}{T}\right)}$$

where H is the heat of formation, and R, the gas constant, $= 1{\cdot}985$ calories per gram molecule.

H was found to be 22,300 calories at 50° C. and 13,400 calories at 30° C.

The heat of formation calculated from Berthelot's value for the heat of combustion of ethylene di-iodide (*Ann. Chim. Phys.* (1900) (7), **21**, 296) and Mixter's value of the heat of combustion of ethylene at constant pressure (*Amer. Journ. Science* (4), **12**, 347 (1901)) is 20,400 calories which is in fair agreement with our value for H at 50° C.

A decrease in the heat of formation from 22,300 calories at 50° to 13,400 calories at 30° is too great to be explained by the presence of two forms of iodine, as this would imply a heat of transformation of 9000 calories.

It is therefore probable that the second suggested explanation is

correct, and that our values of K are inexact below 40° C. owing to the effect of ~~iodine on the vapour pressure of ethylene di-iodide.~~ ethylene or the di-iodide on the vapour pressure of iodine.

V. Kinetics of the Formation and Decomposition of Ethylene Di-iodide.

(*a*) An attempt was made to obtain values of the velocity constant k of the reaction between C_2H_4 and I_2 in the gaseous state by assuming the rate of change of pressures P in the glass-spring manometers of section II to be given by

$$\frac{dP}{dt} = k' \cdot P_{C_2H_4I_2} - k \cdot P_{C_2H_4} \cdot P_{I_2}$$

where $P_{C_2H_4I_2}$ and P_{I_2}, the vapour pressures of $C_2H_4I_2$ and I_2, are constants.

On integration this gives

$$k = \frac{1}{t} \cdot \frac{2{\cdot}303}{P_{I_2}} \log_{10} \frac{P\infty - P_0}{P\infty - P},$$

where $P\infty$ is the equilibrium pressure, P_0 the pressure at time $t = 0$, and P the pressure at time t.

This formula was applied to some of the experimental values of P. The values of k thus obtained were not constant, but showed a steady drift.

The reaction probably takes place on the surface of $C_2H_4I_2$ or I_2 or on the glass walls instead of in the body of the gas. There is evidence of considerable adsorption of ethylene.

A set of readings of P at 26·8° C. and the corresponding values of k are given in Table IV. At 26·8° $P_{I_2} = {\cdot}4$ mm. and $P\infty = 12.5$ mm.

Table IV.

t (minutes)	Pressure. P mm.	k.
0	0·9	
60	1·2	$1{\cdot}2 \times 10^{-3}$
255	2·5	1·6
300	3·1	2·0
360	3·8	2·2
1152	9·0	2·8
1212	9·6	3·1
1800	11·7	4·0
∞	12·5	

(*b*) In order to obtain values of k', the velocity constant of the decomposition of $C_2H_4I_2$ in the gaseous state, small quantities (·01 to ·2 gm.) of $C_2H_4I_2$ were placed in a glass bulb which contained a large surface of amalgamated copper gauze to combine with iodine as soon as it was formed. A mercury manometer was attached to the bulb. The bulb was evacuated with an oil pump, sealed off, and immersed in a 25° thermostat in the dark.

If the decomposition under these conditions were a unimolecular gas reaction, the time-pressure curve would be a straight line from the origin, the slope being equal to k' since $\frac{dP_{C_2H_4}}{dt} = k' . P_{C_2H_4I_2}$. The curves actually obtained are shown in fig 5. The low initial slope is probably due to

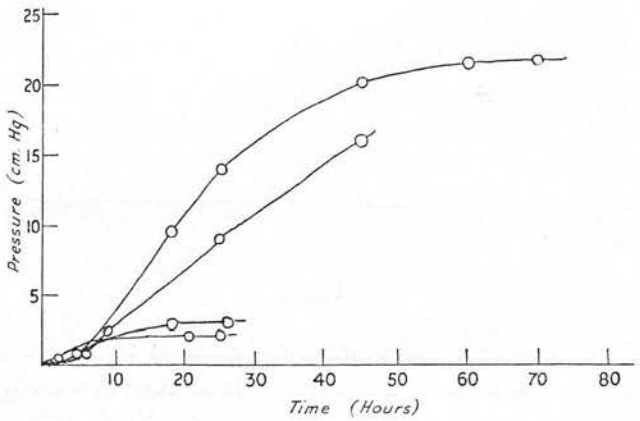


FIG. 5.

adsorption of ethylene on the large surface present in the bulb. The lack of agreement of the slope at the middle part of the curves suggests that the reaction is either a surface reaction or else influenced by traces of the solvent used for recrystallising the ethylene di-iodide, which in these cases was ether. In later experiments carbon tetrachloride was found to be a more suitable solvent.

(*c*) The decomposition of ethylene di-iodide in carbon tetrachloride was studied at 100° C. Tubes containing 11 c.c of solution were sealed up and placed in a water-bath, and titrated with thiosulphate at intervals of a few days.

The reaction was found to be autocatalytic. The I_2 formed by decomposition catalysed the decomposition. Curves I, II, and III in fig. 6 show the decomposition of $\frac{N}{25}$ solutions of ethylene di-iodide in carbon tetrachloride which contained different initial concentrations of

iodine. Solution I contained $\frac{N}{100,000}$ I_2, II contained $\frac{N}{250}$ I_2, and III $\frac{N}{50}$ I_2. The initial slopes of curves I, II, and III are approximately proportional to the square root of the iodine concentration.

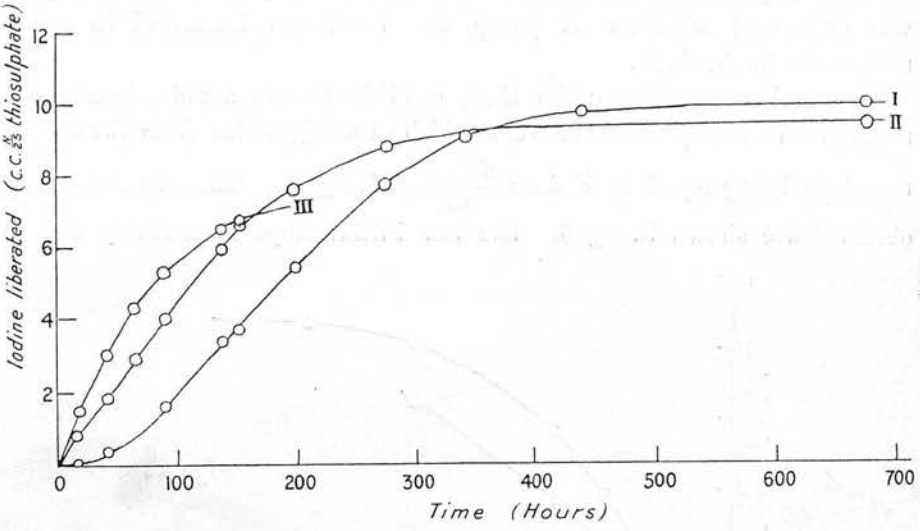


FIG. 6.

Equilibrium constants could not be calculated because figures for the solubility of ethylene in carbon tetrachloride at 100° C. were not available, and therefore the concentration of ethylene in the liquid was not known.

SUMMARY.

The pressure of ethylene in equilibrium with solid iodine and solid ethylene di-iodide was measured at temperatures between 10° and 65° C.

The vapour pressure of undissociated ethylene di-iodide was measured at four temperatures between 15° and 55° C.

From these results and the known vapour pressure of iodine equilibrium constants $k = \frac{(\text{pressure of } C_2H_4) \times (\text{pressure of } I_2)}{\text{pressure of } C_2H_4I_2}$ were calculated.

Some experiments were made on the rate of formation and decomposition of ethylene di-iodide.

We desire to thank Professor Sir James Walker and Professor Kendall for their interest in our work, and Imperial Chemical Industries, Ltd., for a grant towards the cost of apparatus.

(*Issued separately* , 1929.)

[Sent in to the Faraday Society for publication.]

Decomposition of Ethylene by ultra-violet light.

by

R.B.Mooney,M.A.,B.Sc.,& E.B.Ludlam,M.A.,D.Sc.

Submitted in support of Thesis for Ph.D.

Decomposition of Ethylene by ultra-violet light.

Berthelot and Gaudechon [C.R. 150,1169 & 1327] studied the action of the radiation from a mercury vapour lamp on ethylene and acetylene. The gases were enclosed in a quartz reaction chamber to which a mercury manometer was connected. Polymerisation took place, giving rise to a liquid in case of ethylene, and a solid in the case of acetylene.

After the publication in 1922 of a paper by Cario and Franck (Zeit.f.Physik, 11 p.161) on the production of atomic hydrogen by excited mercury atoms, several investigators studied the effect of excited mercury on the polymerisation and hydrogenation of ethylene. (Taylor and Marshall J. Phys. Chem. 29 1141 ; Olson and Meyers: J.A.C.S. 48 389 ; Bates and Taylor J.A.C.S. 49 2439).

The presence of excited Hg atoms in the 2^3P_1 state appeared to be essential. Taylor and Marshall, Olson and Meyers, Bates and Taylor all found that there was no action on ethylene or C_2H_4 - H_2 mixtures containing Hg when the 2536·7 A line of the Hg vapour lamp was reversed.

The experiments of Olson and Meyers and of Bates and Taylor on illumination of ethylene and ethylene hydrogen mixtures containing Hg vapour showed a small initial rise of pressure followed by a large/

large decrease as polymerisation or hydrogenation proceeded. The initial rise is explained by the decomposition of ethylene to give acetylene and hydrogen. Bates and Taylor found acetylene in the gas issuing from the reaction vessel.

The results of these experiments showed that excited mercury atoms have a very great influence on systems containing ethylene, and it appeared that the reactions observed by Berthelot and Gaudechon were dependent on the presence of mercury in the reaction vessel. Bates and Taylor state definitely "Ethylene condenses under the influence of excited Hg atoms with an initial rise in pressure. This does not occur by action of light adone".

In the course of some work on the photochemistry of ethylene and iodine we found ~~that~~ it necessary to investigate the absorption spectrum of ethylene gas. With this object, an absorption cell five feet long, with crystalline quartz ends was used. Ethylene was prepared from ethyl alcohol and phosphoric acid. It was purified by bubbling through silver nitrate and sulphuric acid, liquifying in liquid air, and fractionating. The absorption cell was evacuated with an oil pump and ethylene allowed to fill it at atmospheric pressure. We did not have a suitable source of continuous radiation at our disposal so metallic sparks were used. Photographs were taken with a small Hilger quartz spectrograph, through 5 ft vac. and 5 ft. C_2H_4. We found that absorption was practically complete from 185$\mu\mu$ and 199$\mu\mu$. About 75% of light

of/

of wavelength 202μμ was absorbed and there was slight absorption of 206 and 210μμ . There was no appreciable absorption beyond 213 The absorption was not due to leakage of air into apparatus because 5 feet of air at atmospheric pressure gave only slight absorption at 193μμ and incomplete even at 185μμ .

Our results are in agreement with those of Stark, Steubing, Enklater and Lipp (Jahrb.Radioactiv.Electr. 10, 139) which were not known to us until the above work had been carried out. They used a cell about 25 cm. long. They observed an absorption band at about 195μμ which showed some structure. With our apparatus absorption was so great at 195μμ that no structure could be observed. They found that liquid ethylene absorbs wavelengths as long as 235 μμ.

These results suggested to us that ethylene would be acted on by ultraviolet light even in the absence of mercury vapour, provided care was taken to use light of a wavelength short enough for ethylene toabsorb, viz., appreciably shorter than 210μμ . The experiments of Olson and Meyers, Taylor and Marshall, and Bates and Taylor seem to have been carried out under conditions which would prevent much light of the required wave length from reaching the reaction vessel. Olson and Meyers had three thicknesses of quartz and 30 cm. of air between lamp and ethylene. Bates and Taylor and Taylor and Marshall had a layer of water between lamp and ethylene and one or two thicknesses of quartz. Under these conditions/

conditions the 1849 Hg line would be practically entirely absorbed and there is no other very strong Hg line in the ethylene absorption region. Thus no purely photochemical action is to be expected under the conditions described by these authors.

We decided to carry out some experiments in which light would be used which is strongly absorbed by ethylene. The experiments showed a marked decomposition of the gas, acetylene being one of the products. The experimental arrangements were as follows. Ethylene was obtained from a cylinder of compressed gas. The gas was 97 to 98% ethylene, the balance being mainly hydrogen. It gave no positive test for acetylene. The ethylene was passed through ammoniacal silver nitrate and concentrated sulphuric acid, and over calcium chloride, then through a silica reaction cell with a window of crystalline quartz into a wash-bottle containing either ammoniacal silver nitrate or ammoniacal cuprous chloride.

Ethylene was passed through the apparatus for about 30 minutes atthe rate of 3 bubbles per second. An aluminium spark, excited by 10,000 volts from a transformer and connected in parallel with a condenser, was then placed a few millimetres from the quartz window of the reation chamber. This arrangement gives very intense emission at 186$\mu\mu$. When the spark had been on for 5 - 10 minutes a distinct precipitate of silver azetylide was visible in the final washbottle. Repetition of the experiment with cuprous chloride in place of silver nitrate gave a red precipitate of copper acetylide in/

in 3 - 4 minutes.

Since care had been taken to exclude mercury vapourfrom the apparatus, viz., by cleaning all glass and silica with nitric acid, and using clean, new rubber tubing for connections, the above results prove that the presence of mercury vapour is not essential for the decomposition of ethylene by ultra-violet light.

Berthelot and Gaudechon stated that no acetylene was found in the residual gas when pure ethylene was exposed to ultra-violet light, but that acetylene was obtained when the ethylene initially contained an admixture of oxygen.

In order to test the possibility of our results being due to oxygen impurity, we placed a washbottle containing alkaline pyrogallic acid between the sulphuric acid washbottle and the calcium chloride tube. A slow stream of ethylene was passed through the apparatus for four hours and the sparking was commenced. Acetylene was found as before in the issuing gas.

Experiments in which ethylene was taken from the cylinder through P_2O_5 to the reaction chamber gave similar results.

Further experiments were carried out in which the sources of light were 1) a spark between zinc electrodes and 2) a mercury amalgam lamp containing cadmium zinc bismuth and lead. Both of these light sources gave a fair amount of light on the short wavelength side of 210$\mu\mu$, but much less than the aluminium spark. As was expected, the rate of production of acetylene was much slower, but still considerable. Traces of acetylide could usually be observed in the inlet tube of the washbottle after 15 - 30 minutes illumination.

When/

When a piece of calcspar 3 millimetres thick was placed between the mercury lamp and the quartz window no formation of acetylene could be observed after four hours. Similar negative results were obtained when a quartz cell containing a thickness of 1 centimetre of distilled water was placed between the zinc spark and the quartz window. The calcspar absorbed nearly all light of shorter wavelength than 210$\mu\mu$, and the water cell absorbed light of wavelength 202$\mu\mu$ and shorter. Most of the light which ethylene absorbs was therefore being absorbed by the screens. The water cell let most of the zinc 206$\mu\mu$ line pass through, and as it is appreciably absorbed by ethylene there should be slight decomposition. No doubt if our experiments had been carried ~~out~~ on for longer periods some formation of acetylene would have been observed.

The fact that a zinc spark through quartz decomposes ethylene shows that light of wavelength 202$\mu\mu$ can decompose it, because the zinc spark has no strong line between 202 and the limit of transmission of quartz.

Our results show that light of wavelength 186$\mu\mu$ and 202$\mu\mu$ decomposes ethylene, and it is probable that any light in the region of absorption is capable of decomposing ethylene.

The solid deposit obtained by previous workers was only observed in minute amounts, and was never present on the quartz window in sufficient quantity to slow down the reaction.

This is easily explained on the assumption that polymerisation involves the activation of acetylene molecules formed by the primary decomposition. If a fairly rapid stream of gas is passing through/

through the reaction chamber, the acetylene molecules will be swept away from the range of the radiation and very few of them will have a chance of being activated and causing polymerisation.

The primary photochemical process involved in the action of light on ethylene remains uncertain. It is, however, suggestive that the energy required for the reaction $C_2H_4 \rightarrow C_2H_2 + 2H$ is 135,100 calories, corresponding to a wavelength of 211$\mu\mu$. Our measurements of the long wavelength limit of the absorption of ethylene give 210 - 213$\mu\mu$. In calculating the heat of dissociation of ethylene to acetylene and atomic hydrogen we used the value 100,100 calories for the heat of dissocation of hydrogen (Witmer, Proc.Nat.Acad.Sci. 12, 238).

If the primary photochemical process is a dissociation to acetylene and atomic hydrogen there will be a small concentration of atomic hydrogen in the illuminated gas. An attempt was made to detect its presence by its property of reducing copper oxide, but no reduction was observed. This is not surprising because at the pressure used (760 mm. and 20 mm.) nearly all the atomic hydrogen would have an opportunity of reacting with ethylene before it reached the copper oxide.

Summary.

It has been shown that ethylene is decomposed by light of wavelength shorter than 210$\mu\mu$, giving acetylene as one of the products of decomposition.

The presence of Hg vapour is not essential for the decomposition/

decomposition, contrary to the statement of Bates and Taylor.

The ultraviolet absorption spectrum of ethylene has been studied. The long wavelength limit of absorption viz., 210 - 213 coincides with that calculated from the heat of dissociation of ethylene to acetylene and atomic hydrogen.

Proc. Roy. Soc. Edin.

(d) (4)

The Influence of Air and Moisture on the Budde Effect in Bromine.

By E. B. Ludlam, M.A., D.Sc., and R.B.Mooney, M.A., B.Sc.

In a former paper (Proc.Roy.Soc.Edin. (1924) 44 197) it wasshown by one of us that pure bromine vapour gave no expansion whennexposed to light in the whole range from the visible to the Schumann region. These results were confirmed later by Lewis and Rideal (J.Chem.Soc.,1926 583) working with a mixture of air and bromine vapour. On the other hand Brown and Chapman (J.Chem.Soc. 1928 560) and Matthews (Trans.Faraday Soc., 25 41) found that drying an air-bromine mixture only slightly diminished the Budde expansion, without entirely preventing it. Brown and Chapman, and also Matthews seem to have had the impression that our experiments were conducted on a mixture of air and bromine vapour. On the contrary, considerable care had been taken to remove air, and the bromine vapour could only have contained very small traces of it.

The phosphorus pentoxide we used for drying was specially pure, having been made by Shenstone many years ago and sealed up in a glass tube which had itself been sealed up in a second glass tube. The purified bromine was distilled from some of this and condensed/

condensed in a glass bulb containing more of the pentoxide, the bulb being joined to the silica apparatus by a ground joint. From this bulb it was distilled three times into a silica bulb containing pentoxide, evacuating between each filling and the silica being heated in a bunsen flame, and then the silica apparatus was sealed off. We have no record of how long the liquid bromine was allowed to remain in contact with the phosphorus pentoxide before the apparatus was sealed off from the silica bulb, the latter being kept in melting ice, but it was no lengthy period, probably only a day or two. What is, however, important to emphasize now is that our apparatus, being of silica and admitting of strong heating, was entirely free from the film of adsorbed water which presents the greatest difficulty in extreme drying.

As regards air, it is obvious that there could have been only a trace, for we did not rely merely on pumping but on washing out. It is, however, very much to the point to remark that in work on the emission spectrum of bromine, one of us had noticed how difficult it is to remove the last traces of air from bromine (Ludlam and West, Proc.Roy.Soc.Edin., 44 185). The liquid bromine seemed to retain air in solution. Further it was evident from the intensity distribution in the spectrum that a large proportion of the energy of the bromine was communicated to the extremely minute amount of air. We think that this fact is of importance in the interpretation of the experiments of Brown and Chapman and of Matthews.

In 1924 we concluded that the energy absorbed by the pure bromine/

bromine must be radiated again, probably in the infra-red. The alternative hypothesis, that it had been communicated to the walls of the vessel, was not at that time seriously entertained.

We have now performed an experiment with the object of examining what remained just a bare possibility viz., that the energy was re-radiated in the visible but was not easily observable by the eye. Molecular fluorescence of bromine vapour at a pressure of 6·4 cm. is out of the question, it is only observable at very low pressures. On the other hand the work of Franck and his collaborators does suggest the possibility that light might be radiated as a result of the combination of a normal and an excited bromine atom, which had been produced by the absorption of light of wavelength shorter than 510 $\mu\mu$. It was for this that we looked.

A silica tube 8 cm. long and 1 cm. diameter with plane quartz ends was filled with purified bromine which had been dried over specially purified phosphorus pentoxide. The tube was evacuated by means of a rotary oil pump protected by a soda-lime tower, and was washed out with bromine vapour before being sealed off. The sides of the tube were blackened except for a strip opposite the slit of the spectroscope. Light from a mercury vapour lamp was passed through a condensing lens and then through Wratten filter No.50 which removed nearly all the light except 436 $\mu\mu$. It then passed through a hole in a screen of black paper into the tube. The spectroscope was set at right angles to the beam of light ~~from~~

so/

so that only scattered or re-radiated light from the bromine could enter the slit. Eight hours exposure showed no trace of any such radiation.

From Franck's interpretation of the absorption spectra of the halogens (Trans. Faraday Soc. 21 536) we know that light in the region of continuous absorption (i.e. of wavelength shorter than 510 $\mu\mu$ for bromine) dissociates the halogen molecule into a normal and an excited atom. Light in the region of band absorption produces an excited molecule which can lose its energy in three ways:

(1) by fluorescence,

(2) by deactivation in a collision of the second kind

(3) by dissociation into atoms following a collision.

At pressures which have been used in studying the Budde effect, there is no fluorescence. The time between collisions is much less than the mean life of the excited molecule.

If (2) occurred to any great extent there would be a heating effect in the dry gas, and consequent rise of pressure or expansion. (3) is the only alternative. Therefore at ordinary pressures the final effect of light in the whole absorption region is the same, viz., dissociation of halogen molecules into atoms. The absence of a recombination light shows that the excited atoms lose their energy of excitation in collisions of the second kind. The result of illuminating the vapour of the halogens is to increase the concentration of normal halogen atoms.

This/

This explanation of the effect of light on the halogens at ordinary pressures is confirmed by the work of Jost (Z.phys. Chem., 134 92) on the velocity of formation of HBr in light of different wavelengths. His results show no discontinuity on passing from the region of continuous absorption to that of band absorption. He interprets this as evidence that (1) and (2) do not take place to any marked extent. in Br_2 vapour.

Suggested explanations of the Budde effect.

Three main questions arise from the experimental results:

(a) When bromine is free from air and moisture why is there no expansion? What becomes of the absorbed energy?

(b) Why does moist bromine free from air show the expansion?

(c) Why does dry bromine containing air show the expansion?

Lewis and Rideal attempted to explain the influence of water by postulating a photo-sensitive compound Br_2H_2O, existing mainly on the walls of the vessel. The evidence for the existence of this compound is not convincing, and its existence is not in any case sufficient to explain the inhibition by drying, Lewis and Rideal had also to assume that the dry gas radiates the energy absorbed. In support of this assumption they claimed to be able to detect a slight difference in the light scattered by wet and dry bromine vapour, but as bromine, at the pressures they worked with, gives no scattered or fluorescent light, or practically none, there is little doubt that they were observing light reflected from the sides/

sides of the tube.

Experiments by Mellor (J.Chem.Soc.,1902,1280) and Cordier (Monatsh.,21 660) which indicated a slight difference in the absorption of dry and moist chlorine were not confirmed by von Halban (Z.phys.Chem.,103 71) and Kistiakowsky (J.Amer.Chem.Soc.,49 2194) who concluded that there was practically no difference. The slight difference observed by Mellow and Cordier is certainly not sufficient to serve as a basis for explaining the Budde effect in chlorine.

Any explanation of the Budde effect which involves the emission of radiation by the dry gas is almost certainly incorrect, in view of our experiment with bromine and a similar experiment carried out by Kistiakowsky in the case of chlorine. He found practically no scattered radiation which could effect either a photographic plate or a thermopile.

Kistiakowsky advanced the following explanation of the Budde effect. In the dry gas, halogen atoms are produced, and they recombine on the walls of the vessel. None of the energy of recombination is made available for heating thegas.

In the moist gas, on theother hand, recombination of the atoms, is catalysed by water, and as the reaction takes place in the body of the gas, the energy of recombination heats the gas instead of the walls.

It seems to use that a more probable explanation has been overlooked. The chief difference between absolutely dry bromine vapour and bromine vapour containing a trace of moisture, is that in the second case/

case there is a film of adsorbed water on the walls of the containing vessel. Such a film of water is known to inhibit certain reactions which are catalysed by dry glass. Wood (Proc.Roy.Soc.,1922 [A] 102 1) found that free hydrogen atoms recombine on the surface of dry glass, and that this recombination is very much retarded by a film of adsorbed water. The effect of water on the hydrogen-chlorine reaction has also been attributed to inhibition of the union of hydrogen atoms at the walls. (Bowen, J.Chem.Soc.,1924,1233) Shenstone's observation (J.Chem.Soc.,1897 471) that ozone is stabilized by a trace of moisture may also be due to a similar poisoning of the walls by water.

The influence of water on the Budde effect is capable of the same explanation. Illumination of the dry halogen dissociates some of the molecules into atoms. These can recombine either in the gas in ternary collosions, or on the walls. The fact that dry Br_2 or Cl_2 gives a little or no expansion shows that recombination in ternary collisions, which would heat the gas, does not take place very often. Recombination on the walls heats the walls and not the gas.

In the moist halogen , on the other hand, recombination on the walls is retarded by the film of adsorbed water. The concentration of atoms in the gas rises until ternary collisions become sufficiently frequent to cause recombination of the atoms as quickly as they are formed. The expansion which is observed when the moist halogens are illuminated will be due partly to heat given/

given out by recombination in ternary collisions, and partly to the increased number of particles in the gas.

It is important to know whether the number of atoms striking the walls is sufficiently great to account for the absence of expansion in the dry gas. An approximate calculation has been made of the rate of production of bromine atoms and of the number of atoms which strike the walls per second under the experimental conditions described in the previous paper.

From an inspection of the absorption spectrum of bromine vapour, and of the curve giving the distribution of energy emitted by a black body at 3550° A. it was estimated that the energy absorbed when the bromine was exposed to light from a 200 c.p. lamp at 80 centimetres was approximately 5×10^{-5} watts. Taking 420 $\mu\mu$ as the mean wavelength of light absorbed this gives 10^{14} quanta absorbed per sec. and, or 2×10^{14} Br atoms produced per second. This estimate may be 100 times too great or too small, but scarcely 1000 times.

If the upper limit of the Budde effect in dry Br_2 under these conditions is .02 mm. the upper limit of the partial pressure of Br atoms is .04 mm. Assuming that the distribution of Br atoms is uniform (a not unreasonable assumption in view of the low pressure) the number of bromine atoms which strike the walls (area 6.5 $cm.^2$) works out at 5×10^{19} per second. If one bromine atom combines for every 2.5×10^5 that strike the wall, the removal of atoms from the dry gas can take place fast enough. If the upper limit of the Budde effect is much less than .02 mm., the margin between the number of atoms striking the wall and the number of atoms which combine/

combine at the walls must be correspondingly reduced.

The experimental evidence of the influence of dry air on the Budde effect in bromine is rather uncertain, because of the contradictory results obtained. Lewis and Rideal obtained no expansion on illuminating a dry bromine-air mixture, while Brown and Chapman, and Matthews obtained a very definite expansion. It is difficult to account for the discrepancy. The only obvious difference in the experimental conditions is that Lewis and Rideal used a glass spring gauge, while the others used a differential thermometer arrangement with a thread of bromine as indicator. The results of Brown and Chapman and of Matthews can be explained by saying that the increase in pressure due to addition of air increases the number of ternary collisions leading to recombination, and hence increases the amount of energy available to heat the gas. High pressure will also diminish the number of atoms combining on the walls of the vessel by reducing the rate of diffusion of atoms from the track of the beam of light to the walls.

It has been generally believed that the expansion of the moist gas on exposure to light is due entirely to a heating of the gas, and not at all to dissociation into atoms. The experimental evidence (which is confined to the case of chlorine) does not seem to us to be conclusive either way. (Budde, Pogg.Ann.Ergb., 1874, 6 477; Bevan, Trans.Roy.Soc., 102 [A] 91; Mellor J.Chem.Soc., 1902, 1280). All observations of the rise in temperature of illuminated moist chlorine have been made by means of thermometers placed in the beam/

beam of light, and capable of being directly heated by the light. The rise in temperature is greater when the thermometer is surrounded by chlorine than when it is surrounded by air. This is explained by the fact that the thermal conductivity of chlorine is only one third that of air. There is no experimental evidence to dispose of the possibility that an appreciable part of the expansion may be due to an increased concentration of halogen atoms.

Some points in Matthews' paper call for discussion. He observed a small expansion on illumination of dry bromine vapour. His apparatus consisted of two evacuated bulbs immersed in a thermostat, and connected by a capillary tube containing a thread of liquid bromine which was kept at a temperature below that of the thermostat. The pressure of Br_2 in the bulbs was thus always equal to the vapour pressure of Br_2 at the temperature of the capillary. If the Budde expansion were purely thermal, it would not be possible to observe an expansion, because the pressure would always remain constant no matter how the temperature of the gas in the bulbs varied. On the other hand, a small concentration of Br atoms could produce a marked expansion. This expansion is not resisted by compression of the gas in the dark bulb, because bromine condenses in the capillary to keep the pressure constant. The expansion for a given pressure increase is greatly magnified as compared with that registered when the bulbs contain air as well as bromine.

On these grounds it is not possible to affirm that there is any real contradiction between Matthews' result and that given in/

in our previous paper.

If, even when the increased sensitiveness of Matthews' arrangement in the absence of air is taken into account, his ~~pressure-increase~~ result should still indicate a pressure increase of more than .02 mm., it is possible that the film of phosphorus pentoxide which covered the walls of his reaction vessel may explain the discrepancy. A layer of pentoxide might resemble a layer of water in preventing recombination. It is known that a layer of NaCl prevents the breaking of the Nernst chain in the hydrogen chlorine reaction.

Repetition of Matthews' experiment, using both wet and dry bromine, would show whether the concentration of Br atoms is greater in moist than in dry bromine exposed to light. This would decide between Kistiakowsky's explanation of the Budde effect and that put forward in this paper. If the recombination in the body of the gas is catalysed by water, the concentration of Br atoms in the moist gas will be less than in the dry gas. The opposite effect will be observed if the role of water is to poison the walls of the vessel.

Summary.

A survey is given of recent work on the action of light on bromine vapour, both dry and in presence of air and moisture.

Suggested explanations of the facts are discussed. It is concluded that the influence of water is due to a "poisoning" of the walls of the vessel, which prevents them from catalysing the recombination of bromine atoms.